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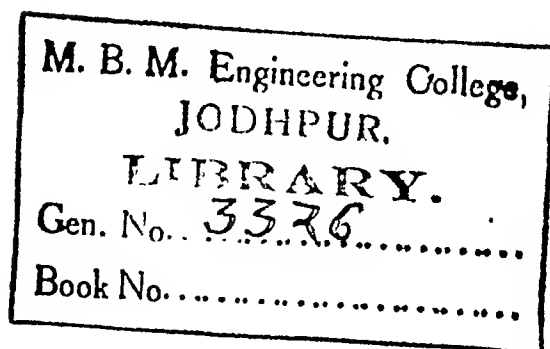
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With an index by Dr. J. N. Goldsmith

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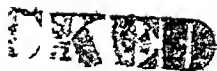
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## NOTE

Italicised words in inverted commas may be registered trade names.

Of these industrial gases, only town's gas is produced primarily as a fuel. The others are used incidentally as such, notably coke-oven gas, which is generally employed to heat the settings, but is sometimes utilised also as a source of hydrogen; cracker gas is an important source of olefins.

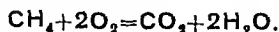
In connection with the synthesis of ammonia, coke-oven gas (cf. Vol. III, 268c) is separated by refrigeration (e.g., in the Linde-Bronn plant) with the formation of a liquid rich in methane (ca. 75%). This is normally re-evaporated and used as a fuel to heat the settings, but it could, in principle, be diverted to more profitable uses. The separation of methane from mixtures containing 30% or less, either by refrigeration or by solvent extraction might, in itself, prove to be uneconomic, in which case the initial methane content could be raised by a catalysed union of carbon monoxide and hydrogen, which, in coal gases, are the principal constituents other than methane. By a similar reaction, the synthesis of methane from gases of the water-gas type could be effected (v. Vol. II, 349c). Present tendencies in the Gas Industry, in the direction of the total gasification of coal, indicate the ultimate production of a gas rich in methane by a combination of carbonisation and hydrogenation processes.

Unlike certain other potential fuels (e.g., alcohol, benzene) methane is not in great demand for chemical synthesis. The manufacture of carbon black is perhaps the only technical purpose for which it is at all widely used. Indeed, owing to its inactivity, it seems unlikely that methane will be employed to a great extent in chemical industry, and the world's vast resources can therefore be assumed to be potentially available as fuel.

It has been suggested that methane, by catalytic hydrolysis to water gas, followed by a Bergius or Fischer-Tropsch synthesis, might be converted to petrol. In this article however, only the application for fuel purposes of methane, as such, will be considered.

#### COMBUSTION PROPERTIES.

Methane reacts with twice its own volume of oxygen when completely converted to carbon dioxide and water.



The theoretical mixture with air therefore contains 9.47% of methane. Hydrogen and carbon monoxide (hence coal gas also) require less air for complete combustion but all gaseous hydrocarbons require more.

The concentration range of inflammability in air (ca. 5-15%) is considerably wider than that of petroleum (ca. 2-5%) and other hydrocarbon fuels, but narrower than that of hydrogen (ca. 4-75%) or carbon monoxide (ca. 13-75%), or fuels rich in these gases (town's gas, producer gas).<sup>4</sup> This characteristic is reflected in the mixture range available in engines.

The minimum temperature of ignition of methane so far observed is about 650°C. This corresponds to a considerable lag and probably represents the lowest temperature of any source capable of igniting the gas. Localised sources

require higher temperatures, depending upon their shape and size. Methane is thus more difficult to ignite than petrol (v. Vol. IV, 420).

The net calorific value of methane is 12,000 kg.-cal./kg. (22,000 B.T.U./lb.), as compared with 10,710 kg.-cal./kg. for iso-octane and 10,600 kg.-cal./kg. for No. 1 petrol. In the gaseous state the volumetric calorific value (895 B.T.U./cu. ft. at 60°F. and 30 in. of mercury, saturated with water vapour) is very high, and in the liquid form a value of 100,000 B.T.U./gallon compares with 136,000 B.T.U./gallon for petrol. A gallon of liquid methane weighs 4.3 lb. and yields approximately 100 cu. ft. of gas at normal temperature and pressure. The specific gravity of the gas is 0.55 referred to air as unity.

Under comparable conditions the maximum speed of flame propagation for methane in air is similar to that for carbon monoxide, but it is greatly exceeded by that for hydrogen.<sup>5</sup> Thus methane can replace town's gas in appliances, if the aeration is suitably increased, without danger of "striking back." The tendency to "blow-off" may be increased, however. Since the flame speeds of other hydrocarbons are also greater than that of methane, it can be said that when issuing rapidly from a container through a small orifice, methane is one of the most difficult fuels to ignite.

Methane is a "non-knocking" fuel for internal combustion engines, and can be employed at very high compression ratios. Ricardo<sup>11</sup> has found a H.U.C.R. with methane of 14.5:1 under conditions which with iso-octane gave 11:1. It has probably the highest knock-rating of all fuels.

Like all gaseous fuels, methane has the advantage of good distribution in internal combustion engines and shows no tendency to dilute the lubricating oil. As a consequence of good distribution, gaseous fuels yield an exhaust gas of low carbon monoxide content, and by comparison with heavier hydrocarbons methane gives little carbon deposition. By comparison with producer gas also, it is a "clean" engine fuel.

#### STORAGE.

For purposes of transport and storage methane can be accommodated:

- (i) at low pressure, in gas-bags, semi-rigid containers, or gas holders;
- (ii) compressed into gas cylinders, with or without the use of adsorbent materials;
- (iii) as a liquid at atmospheric pressure in containers vacuum-jacketed or lagged with insulating material. (Since its critical temperature is -82°C., methane cannot exist in the liquid form at normal temperatures.)

These three general methods increase in compactness in the order given. Thus, 1 g. of methane occupies 1,520 c.c. at 25°C. and atmospheric pressure, 6.3 c.c. at 3,000 lb. per sq. in. and 25°C., and 2.35 c.c. in the liquid form at atmospheric pressure. The cumbersome character of the first method is emphasised by these figures.

The most suitable pressure at which to store

and elsewhere, and in the vicinity of the great oilfields of the world the abundant supplies of natural gas are put to domestic uses. However, where unlimited supplies are not available, it appears inadvisable to employ so excellent a fuel as methane in an indiscriminate manner; it is better used (*e.g.*, in the liquid form) as a "calorific reservoir" for the enrichment of gas of low calorific value, in the way, for instance, in which oil gas is at present employed in some countries.

**Engine Fuel.**—The use of methane as a fuel for internal combustion engines is an application which takes advantage of most of its valuable qualities. When employed in a suitably designed engine it is superior to petrol, and as used in a petrol engine it is probably the best substitute fuel available. It has not been widely utilised in this way, however, presumably owing to difficulties of handling. In Germany, compressed sewage gas, and in Italy compressed natural gas, have been employed fairly extensively, and in Great Britain a certain amount of sewage gas is in use. It is reported that methane separated from coke-oven gas by the Linde-Bronn process has been applied as an automotive fuel in Germany. In America, natural gas is not much employed in this way owing to the abundance of petroleum. The application of liquid methane is scarcely beyond the experimental stage, but the technique has been worked out by Egerton<sup>11, 12</sup> in England and it is said that a full-scale scheme has been tried in Russia.<sup>9</sup> In the admixed state (*e.g.*, as town's gas) it has, of course, been more widely applied.

In common with gaseous engine fuels, methane suffers the theoretical disadvantage of low volumetric efficiency as compared with liquids. In practice, however, since a certain amount of induction heating is generally employed to give good distribution with a liquid fuel, and such measures are not needed with a gas, the comparison becomes more favourable to methane, and by a suitable application of the liquid form the disadvantage can be entirely reversed.

Under the same engine conditions, the thermal efficiency with methane is greater than with petrol, an advantage which is increased by utilising the higher compression-ratios available in the former case. In the same way, the slight loss of power consequent upon using methane in a petrol engine can be redressed by an increase of compression ratio.

Owing to the wasteful way in which petrol is necessarily fed to an engine, methane is much more economical for short-delivery service. It has been found that, although the calculated equivalent of petrol to methane is 1:1.5 gallons, owing to superior distribution the figures are about 1:1.4 in continuous running, and (owing to the consideration mentioned above) approach 1:1.2 on a "start-and-stop" service.

The application to an engine of methane from low-pressure storage is not difficult. In the case of a suction intake a slight throttling effects the necessary pressure reduction, whilst for a positive-pressure feed, the gas is led directly to the fuel pump.

In the case of high-pressure storage (3,000 lb.

per sq. in.) the pressure reduction is effected by regulators in two stages,<sup>10</sup> the intermediate pressure being of the order of 10 lb. per sq. in. When the fuel is stored in the liquid form a number of methods are available. The most obvious is to convert the liquid to gas before conveying it to the engine, by means either of a heater in the storage tank, or of an evaporating device to which the liquid is led under controlled conditions, and in which it is evaporated by the hot exhaust gases, or otherwise. A fundamental objection to these schemes lies in the fact that the refrigeration capacity of the cold fuel is not usefully employed. It is clear that this property, if suitably directed, allows of an increase of volumetric efficiency either by injecting the liquid into the air supply or by allowing heat exchange, whereby the intake air supplies the latent heat of evaporation of the fuel.

In any arrangement in which the methane reaches the engine in the form of a gas, a gas-air mixer of conventional design (*see, e.g.*,<sup>10</sup>) may be employed, a suitable adjustment of the mixture strength being made.

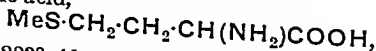
It would appear, however, that advantages should be gained by adopting alternatives to the ordinary suction-intake cycle. Thus, the volumetric efficiency can be improved by employing a pressure-injection system with ordinary spark-ignition engines; and, as Clarke<sup>10</sup> has shown in the case of coal gas, by operating on the Otto cycle at a high compression-ratio, with gas injection during the compression stroke, followed by spark-ignition, a considerable increase in power is derived. A further proposal is to work on the Diesel cycle, drawing in a methane-air mixture on the suction stroke and injecting a small amount of oil, sufficient to initiate ignition, during compression.

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J. H. B.  
**"METHEDRINE."** *d*- $\alpha$ -Phenyl- $\beta$ -methylaminopropane. For treatment of narcolepsy (*v.* SYNTHETIC DRUGS).

S. E.  
**METHINE BASES** (*v.* Vol. II, 481a, b).  
**METHIONINE**,  $\gamma$ -methylthiol- $\alpha$ -amino-butyric acid,



m.p. 283° (decomp., after shrinking at 278°),  $[\alpha]_D^{25}$  -6.87° (in water), is one of the more recently discovered, and is, quantitatively at least, the most important sulphur-containing amino-acid in ordinary diet, and in proteins apart from



metals are converted into organometallic compounds, e.g.,  $\text{PbMe}_4$ ,  $\text{ZnMe}_2$ ,  $\text{HgMe}_2$ ,  $\text{AsMe}_3$ , etc.

Brief accounts follow of the following methyl compounds: amines; cyanide, isocyanide, isocyanate, thiocyanate, isothiocyanate, ethers; halides; nitrite, nitrate; sulphides, sulphites, sulphates, sulphonates; methylene compounds.

#### METHYLAMINES.

Formula	Mono-methyl-amine.	Di-methyl-amine.	Tri-methyl-amine.
F.p.	$\text{NH}_2\text{Me}$	$\text{NHMe}_2$	$\text{NMe}_3$
B.p.	$-92.5^\circ$	$-96^\circ$	$-117.2^\circ$
$\rho$	$-6.7^\circ$	$7.2-7.3^\circ$	$3.2-3.8^\circ$
	0.699	0.6865	0.6709
	$(-10.8^\circ)$	$(-5.8^\circ)$	$(0^\circ)$
Crit. temp.	$156.9^\circ$	$164.6^\circ$	$160.5^\circ$
Crit. pressure	73.6 atm.	164.6 atm.	41 atm.
Basic dissociation constant	$5 \times 10^{-4}$	$7.4 \times 10^{-4}$	$7.4 \times 10^{-5}$
M.p. of $\text{B.HCl}$	$225-226^\circ$	$171^\circ$	$277-278^\circ$
M.p. of $\text{B.HBr}$	$250-251^\circ$	$133.5^\circ$	$243-245^\circ$
M.p. of $\text{B.HI}$	$260-270^\circ$	$155^\circ$	$263^\circ$
M.p. of $\text{B.HNO}_3$	$99-100^\circ$	$74^\circ$	
M.p. of picrate.	$215^\circ$	$158^\circ$	$216^\circ$
Acetyl deriv.	M.p. $28^\circ$ B.p. $206^\circ$	B.p. $165^\circ$	None
Benzoyl deriv.	M.p. $80^\circ$	M.p. $41^\circ$ B.p. $255^\circ$	None

All are colourless gases at room temperature, with characteristic odours, that of methylamine and dimethylamine being ammoniacal, and that of trimethylamine rather more fishy. They are inflammable, burning with yellow flames. Methylamines are very soluble in water to give strongly alkaline solutions, and are more basic than ammonia (basic dissociation constant  $2 \times 10^{-5}$ ). One volume of water dissolves 1,153.9 volumes of methylamine at  $12.5^\circ$ , and 959 volumes at  $25^\circ$ . Hydrates described are  $\text{NH}_2\text{Me} \cdot \text{H}_2\text{O}$ , a liquid with  $\rho^{13.9}$  0.8993, and  $\text{NH}_2\text{Me} \cdot 3\text{H}_2\text{O}$ , m.p.  $-35.8^\circ$ ;  $\text{NHMe}_2 \cdot \text{H}_2\text{O}$ , a liquid  $\rho^{13.6}$  0.8126 and  $\text{NHMe}_2 \cdot 7\text{H}_2\text{O}$ , m.p.  $-16.85^\circ$ ;  $\text{NMe}_3 \cdot 11\text{H}_2\text{O}$ , m.p.  $5.34^\circ$ .

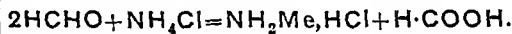
Several of the methods of preparation give mixtures, and various methods are available for the separation of mixtures of two or more members of the series consisting of ammonia and the three methylamines. On a small scale the four can be separated by Bertheaume's method (Compt. rend. 1910, 150, 1251), viz. conversion into the hydrochlorides, evaporation to dryness, and treatment with dry alcohol-free chloroform, which dissolves out dimethylamine and trimethylamine hydrochlorides. These are dissolved in 2,000 parts of water after removal of the chloroform, and trimethylamine precipitated as the sparingly soluble periodide  $\text{NMe}_3\text{I}_2$ , m.p.  $66^\circ$  (Delépine, Ann. chim. 1896, [vii], 8, 452) by a solution of iodine in potassium iodide. The chloroform-insoluble ammonium chloride and methylamine hydrochloride mixture is separated by treating in solution with mercuric oxide in the presence of sodium hydroxide and carbonate, when the ammonia is absorbed and methylamine left in solution (Erdmann, J. Biol. Chem. 1910, 8, 41). Alternatively, the mixture of methylamines and ammonia can be treated with formic or higher fatty-acids or their esters to give amides, and the unchanged trimethylamine removed, whilst the amides (e.g., formamides) can be separated by fractional

distillation and the amines recovered by hydrolysis (U.S.P. 2310478; G.P. 454459). On a large scale, separation of the amines can be achieved by fractional distillation under normal, or more usually, increased pressure, but complications occur owing to the formation of various azeotropic mixtures, although the composition of these can be varied by changing the pressure (e.g., for methylamine-trimethylamine mixtures, see U.S.P. 2126600). Other methods involve the use of solvents, e.g., trimethylamine and ammonia can be separated by selectively absorbing the trimethylamine in organic solvents or solutions of inorganic salts (U.S.P. 2125905; B.P. 475818). Ammonia can be removed from trimethylamine-ammonia mixtures by addition of an inert substance (e.g., an ether or  $\text{C}_4$  aliphatic hydrocarbon) which is capable of forming with ammonia a binary azeotropic mixture of lower boiling-point than that of the trimethylamine-ammonia azeotrope (U.S.P. 2091636). (See also Annual Rep. Prog. App. Chem. 1938, 23, 139.)

For general reactions of methylamines, v. AMINES, Vol. I, 312b.

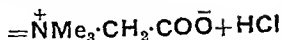
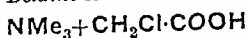
**Methylamine,  $\text{NH}_2\text{Me}$ .**—Occurs in certain plants as *Mentha aquatica* L., *Mercurialis perennis* L., *M. annua* L., and *Leptotænia dissecta*. It has also been found in the flesh of the coot (*Fulica atra*), in herring brine, in crude wood spirit, and among the products of dry distillation of sugar-beet molasses.

A convenient preparation is by the interaction of formaldehyde and ammonium chloride:

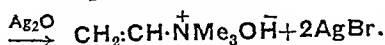
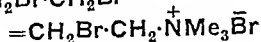
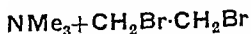


The yield is 45–50% of theory (Organic Syntheses, Coll. Vol. I, 1941, p. 347). Methods have been developed for the production of methylamine from methyl alcohol and ammonia by passage over various catalysts, e.g., aluminium silicate (U.S.P. 1875747), charcoal and alumina (U.S.P. 2017051), or alumina gel in a tube lined with manganese-copper alloy at  $380^\circ/80$  atm. (B.P. 422563). Turner and Howald prepared methylamine in 55% yield by 8 hours' heating, at  $300^\circ$  in an autoclave, of a mixture of methyl alcohol, ammonium chloride, and zinc chloride (J. Amer. Chem. Soc. 1920, 42, 2663). The numerous other methods of preparation include reduction of hydrogen cyanide with hydrogen in the presence of the cyanides of hydrogenating metals (U.S.P. 2072247); reduction of chloropiricin with iron and acetic acid (Geisse, Annalen, 1859, 109, 282); reduction of hexamethylenetetramine with zinc and hydrochloric acid (G.P. 73812); electrolytic reduction of nitromethane (Pierron, Bull. Soc. chim. 1899, [iii], 21, 783); reduction of methyl nitrite (Gaudion, *ibid.* 1910, [iv], 7, 824); reduction of formaldoxime (Takaki and Ueda, J. Pharm. Soc. Japan. 1938, 58, 276); action of ammonia on methyl iodide (Hofmann, Annalen, 1851, 79, 16); action of ammonia on methyl chloride (Vincent, Chappuis, Bull. Soc. chim. 1886, [ii], 45, 499); action of ammonia on dimethyl sulphate (Denham and Knapp, J.C.S. 1920, 117, 236); Hofmann degradation of acetamide with bromine and alkali (Hofmann, Ber. 1882, 15,

Betaine is formed with chloracetic acid:



and neurine with ethylene dibromide:



Trimethylamine Oxide,  $\text{NMe}_3\text{O}$ , is widely distributed in fish and animal tissues (Kapeller-Alder and Krael, *Biochem. Z.* 1930, 224, 364). It may be prepared by the action of methyl iodide on hydroxylamine, or better, by treatment of trimethylamine with 3% hydrogen peroxide at room temperature (Dunstan and Goulding, *J.C.S.* 1899, 75, 792, 1004). On heating, formaldehyde and dimethylamine are formed:

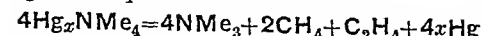


It separates from water as the dihydrate, m.p. 255–257°. The anhydrous compound forms needle-shaped crystals, m.p. 96°.

**Tetramethylammonium Compounds.**—*Tetramethylammonium Iodide* is formed by the addition of methyl iodide to trimethylamine, and is the chief product from the action of ammonia on an excess of methyl iodide (Hofmann, *Proc. Roy. Soc.* 1851, 381). It is a crystalline substance, soluble in hot water, sparingly so in cold, and decomposes on heating above 230°. The chlorine and bromine compounds are similar. When the iodide is treated with moist silver oxide, or the chloride with potassium hydroxide in methanol, the free base, *tetramethylammonium hydroxide*,  $\text{NMe}_4\cdot\text{OH}$ , is formed. It forms a pentahydrate, m.p. 62–63°, a trihydrate, m.p. 59–60°, and a monohydrate which decomposes without melting at 130–135° to give methyl alcohol and trimethylamine. The hydroxide is a strong, hygroscopic base, which absorbs carbon dioxide from the air and will saponify fats. It forms salts with acids.

Tetramethylammonium salts form a series of complex polyhalides of the type  $\text{NMe}_4\cdot\text{X}_x$  where  $x$  is 3, 5, or 7 (e.g., Chattaway and Hoyle, *J.C.S.* 1923, 123, 654).

A solution of free *tetramethylammonium* has been obtained by treating tetramethylammonium chloride with metallic lithium in liquid ammonia. Tetramethylammonium amalgam has been prepared by the electrolysis at –35° of tetramethylammonium chloride in alcoholic solution, using a mercury cathode. It is unstable and decomposes rapidly, probably according to the equation:



(McCoy and West, *J. Physical Chem.* 1912, 16 261).

**Methyl Cyanide** (Acetonitrile, Cyano-methane),  $\text{MeCN}$ .—A colourless liquid, b.p. 81.6°, f.p. –44.9°,  $d_4^{20}$  0.7828, with a pleasant ethereal odour, miscible with water, from which it separates on the addition of sodium chloride. It burns with a luminous flame with a peach-red-coloured edge.

It may be prepared by distilling ammonium acetate or acetamide with phosphorus pentoxide (Dumas, *Compt. rend.* 1847, 25, 383); from aqueous potassium cyanide and dimethyl sulphate (Walden, *Ber.* 1907, 40, 3215); from methyl iodide and aqueous potassium cyanide (Henry, *Compt. rend.* 1887, 104, 1181); by the decarboxylation of cyanoacetic acid at 165° (Van't Hoff, *Ber.* 1874, 7, 1383); by passing acetic anhydride and ammonia over alumina at 500–600° (Van Epps and Reid, *J. Amer. Chem. Soc.* 1916, 38, 2130); and by the passage of methyl alcohol and hydrogen cyanide vapours over a catalyst (G.P. 463123). It is among the products formed by passing acetylene and ammonia over a catalyst at 350° (G.P. 295276); it has also been prepared by numerous other methods.

Methyl cyanide is a good solvent for many organic compounds and forms numerous addition compounds with acids and metallic salts.

**Methyl isoCyanide** (Methylcarbylamine, *iso*Acetonitrile, *iso*Cyanomethane),  $\text{MeNC}$ .—A liquid, b.p. 59.6°, f.p. –45°, with a very unpleasant odour and burning with a bluish-green flame; it explodes readily, is extremely poisonous, and is soluble in 10 parts of water at 15°.

It can be prepared by heating methyl iodide with silver cyanide at 120° and decomposing the resulting addition compound,  $\text{MeNC}\cdot\text{AgCN}$ , with potassium cyanide solution (Gautier, *Ann. Chim. Phys.* 1869, [iv], 17, 215). A large number of addition compounds with metallic salts are known.

**Methyl isoCyanate**,  $\text{MeNCO}$ .—A liquid, b.p. 43–45°, with a pungent odour, prepared from potassium cyanate and dimethyl sulphate in the presence of lime (Slotta and Tschesche, *Ber.* 1927, 60 [B], 298), or from methyl iodide and silver cyanate (Polonovski and Nitzberg, *Bull. Soc. chim.* 1916, [iv], 19, 29). Readily polymerises to trimethylisocyanuric acid. Methyl cyanate is not known.

**Methyl Thiocyanate**,  $\text{MeCNS}$ .—A liquid, b.p. 130°, f.p. –51°, prepared from dimethyl sulphate and barium thiocyanate (Schmitz, *Chem. Zentr.* 1913, II, 1348) or from potassium thiocyanate and calcium methyl sulphate (Musparratt, *Annalen*, 1848, 65, 259). On heating to 180° it is partly converted into methyl *iso*-thiocyanate.

**Methyl isoThiocyanate** (Methyl mustard oil),  $\text{MeNCS}$ .—A white crystalline solid, m.p. 35–93°, with an odour similar to that of horseradish. It is prepared from methylamine and carbon disulphide (Delépine, *Bull. Soc. chim.* 1908, [iv], 3, 642).

**Dimethyl Ether**,  $\text{Me}_2\text{O}$ .—A colourless gas with an ethereal odour, f.p. –138.5°, b.p. –23.6°, sp.-gr. of gas 1.617 (air=1), flash point –41°; burns with a slightly luminous flame. One volume of water dissolves 37 volumes of the gas at 18°. It is readily prepared by heating methyl alcohol with conc. sulphuric acid (Erlenmeyer and Krichbaum, *Ber.* 1874, 7, 699) or with phosphoric acid (Newth, *J.C.S.* 1901, 79, 917). The dehydration of methyl alcohol may be carried out in the vapour phase by passing over heated pumice soaked in sulphuric acid (Senderens, *Compt. rend.* 1931, 192, 1335). On

bromide and sulphuric acid (Bygdén, J. pr. Chem. 1911, [ii], 83, 422), or from methyl alcohol, bromine and red phosphorus (Pierre, Ann. Chim. Phys. 1845, [iii], 15, 373). Methods for large-scale preparation include the passage of methyl alcohol vapour and hydrogen bromide over activated charcoal and phosphoric acid at 280–320° (G.P. 478126).

Methyl bromide is used as a fire extinguisher, for which purpose it is usually kept in sealed vessels under constant pressure and released by the destruction of the sealing device (*v.* FIRE EXTINCTION, Vol. V, 209d). The vapour is poisonous and can be detected by a halide detector lamp (Anon., Amer. Chem. Abstr. 1941, 35, 1355). It has been employed as a fumigant (Andrews *et al.*, *ibid.* 1943, 37, 3550) (*v.* FUMIGATION, Vol. V, 397a). It is effective as a non-inflammable rodenticide (Berry, Bull. Dept. Agric. Calif. 1938, 27, 172). It can be used as a methylating agent (Lucas and Young, J. Amer. Chem. Soc. 1929, 51, 2535) and has been suggested for use as a refrigerating agent (U.S.P. 1547202).

Methyl iodide (iodomethane), MeI.—A colourless liquid with a sweet ethereal odour, m.p. –66–45°, b.p. 42.4°/760 mm.,  $\rho_4^{20}$  2.3346,  $\rho_4^{21}$  2.25102,  $n_D^{21}$  1.5293. A brown colour due to the separation of iodine develops slowly on exposure to light, and this may be greatly retarded by the addition of a drop of mercury. Soluble in about 50 parts of water.

Convenient methods of preparation are from methyl alcohol, iodine, and a mixture of red and yellow phosphorus (Organic Syntheses, Coll. Vol. II, 1943, p. 399), and from potassium iodide and dimethyl sulphate at 60–70° in the presence of calcium carbonate (*ibid.*, p. 404). Both methods give yields of 90–95% of theory. Other methods of preparation include the slow distillation of methyl alcohol and a large excess of constant-boiling hydriodic acid (Norris, Amer. Chem. J. 1907, 38, 639), interaction of aqueous potassium iodide and methyl *p*-toluenesulphonate (Peacock and Menon, Quart. J. Indian Chem. Soc. 1925, 2, 240; Rodionov, Bull. Soc. chim. 1926, [iv], 39, 323), and the electrolysis of aqueous potassium acetate in the presence of iodine or potassium iodide (Kaufer and Herzog, Ber. 1909, 42, 3860).

Methyl iodide is widely used in the laboratory, especially as a methylating agent, owing to the reactive nature of the iodine, and because, being a liquid at room temperature, it is often more convenient than the gaseous chloride or bromide. For large-scale work it is usually replaced by a cheaper methylating agent such as methyl chloride, bromide, or sulphate. Many tertiary bases form crystalline methiodides with methyl iodide which may be used for characterisation purposes. It is used in microscopy because of its high refractive index. When methyl iodide is applied to the skin and covered by impervious material, blisters may result, and methyl iodide can be used in medicine externally as a counter-irritant in neuralgia and sciatica.

Methyl Nitrite, MeO·NO.—A gas, b.p. –12°, prepared from equimolecular quantities of methyl alcohol and isoamyl nitrite (Bertoni,

Gazzetta, 1882, 12, 438), or from sulphuric acid, methyl alcohol, and sodium nitrite (Slater, J.C.S. 1920, 117, 588).

Methyl Nitrate, MeO·NO<sub>2</sub>.—A liquid, b.p. 65°, prepared from methyl alcohol, potassium nitrate, and sulphuric acid (Delépine, Bull. Soc. chim. 1895, [iii], 13, 1044), or from methyl alcohol, urea nitrate, and nitric acid (Lea, Jahresber. 1862, 387). It explodes violently when struck, or when heated to 150°.

Methyl Hydrogen Sulphide (methyl mercaptan, thiomethylalcohol methanethiol, mercaptomethane), MeSH (*v.* MERCAPTANS, Vol. VII, 561a).

Dimethyl Sulphide (dimethyl thioether), Me<sub>2</sub>S.—A colourless liquid with a disagreeable odour, f.p. –83°, b.p. 37.5–38°,  $\rho_4^{21}$  0.8458. Is prepared from sodium methyl sulphate and conc. aqueous potassium sulphide solution (Beckmann, J. pr. Chem. 1878, [ii], 17, 453). Addition compounds are formed with many metallic salts, *e.g.*, 2Me<sub>2</sub>S·P<sub>2</sub>Cl<sub>4</sub>, m.p. 159°, 2Me<sub>2</sub>S·3HgCl<sub>2</sub>, m.p. 150°, etc., and crystalline compounds Me<sub>2</sub>SBr<sub>2</sub> and Me<sub>2</sub>SI<sub>2</sub> with bromine and iodine. With methyl iodide, trimethylsulphonium iodide, Me<sub>3</sub>SI, is formed at room temperature as a crystalline solid, from which the free base, trimethylsulphonium hydroxide, Me<sub>3</sub>S·OH, can be obtained. Oxidation of dimethyl sulphide with nitric acid gives dimethyl sulfoxide, Me<sub>2</sub>SO, and dimethyl sulphone, Me<sub>2</sub>SO<sub>2</sub>, according to conditions (Saytzeff, Annalen, 1867, 144, 150).

Dimethyl Disulphide, MeS·SMe.—A liquid, b.p. 116–118°, prepared by the oxidation of methyl hydrogen sulphide (Cahours, Annalen, 1847, 61, 92).

Methyl Hydrogen Sulphite (methyl sulphurous acid), MeO·SO<sub>2</sub>·OH.—The salts are prepared by the action of sulphur dioxide on alkali methoxides in methyl alcohol (Rosenheim and Leibknecht, Ber. 1898, 31, 409), or by the passage of dry ammonia and sulphur dioxide into absolute methyl alcohol (Goldberg and Zimmermann, Z. angew. Chem. 1902, 15, 901).

Dimethyl Sulphite, (MeO)<sub>2</sub>SO.—A liquid with an acetone-like odour, b.p. 126°, prepared by the action of thionyl chloride or sulphur monochloride on methyl alcohol (Carius, Annalen, 1859, 111, 97; 110, 219). It is isomeric with the methyl ester of methanesulphonic acid, MeSO<sub>2</sub>·OMe.

Methyl Hydrogen Sulphate (methyl sulphuric acid), MeO·SO<sub>2</sub>·OH.—Oily liquid, which does not solidify at –30°, very soluble in water and completely miscible with ether, although the monohydrate is ether-insoluble. It is prepared from equimolecular amounts of methyl alcohol and sulphuric acid at temperatures below 100° (Dumas and Péligot, Ann. Chim. Phys. 1835, [ii], 58, 19). It also results from the action of methyl alcohol with sulphur trioxide below 0° (G.P. 133542), or with chlorosulphonic acid (Claesson, J. pr. Chem. 1879, [ii], 19, 231). The salts are usually prepared by adding the hydroxide or carbonate of a metal to the sulphuric acid–methyl alcohol reaction mixture. The acid chloride, MeO·SO<sub>2</sub>Cl, is usually called methyl chlorosulphonate; it is a

may be prepared by the reduction of chloroform with zinc and hydrochloric acid (Greene, *Compt. rend.* 1879, 89, 1077), or by the chlorination of methane (e.g., McBee, Hass, Neher, and Strickland, *Ind. Eng. Chem.* 1942, 34, 296) or of methyl chloride (G.P. 444799 and 503716).

It may be employed as a local anaesthetic, and as a refrigerant, and is widely used as a solvent and as a degreasing fluid, the vapours not being inflammable or explosive in air.

Treatment with sodium iodide in methyl alcohol gives *methylene chloriodide*, b.p. 109°, which if treated with bromine gives *methylene chlorobromide*, b.p. 68–69°.

**Methylene Bromide** (dibromomethane),  $\text{CH}_2\text{Br}_2$ .—A liquid, b.p. 96.5–97.5°, prepared by the reduction of bromoform with sodium arsenite and caustic soda (*Organic Syntheses*, Coll. Vol. I, 1941, p. 357); from bromine and methylene iodide (Butlerow, *Annalen*, 1859, 111, 251); or from methyl bromide and bromine at 250° (Steiner, *Ber.* 1874, 7, 507). *Methylene bromiodide*,  $\text{CH}_2\text{BrI}$ , b.p. 138°, can be prepared from methylene iodide and iodine bromide.

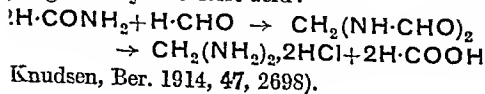
**Methylene Iodide** (di-iodomethane),  $\text{CH}_2\text{I}_2$ .—A yellowish liquid at room temperature, b.p. 180°,  $\rho_{25}^{15}$  3.3326,  $n_D^{15}$  1.7559. The density is the highest of any known organic compound, and for this reason methylene iodide is used for separating mixtures of minerals by flotation, in which benzene or ether may be used as a diluent. Two solid forms are known, an unstable one, f.p. 5.54°, and a stable one, f.p. 6.01° (Stone, *J. Amer. Chem. Soc.* 1932, 54, 112). Solubility in water 1.565 g. per 100 g. at 0°, and 1.446 g. per 100 g. at 10°. Best prepared by the reduction of iodoform with sodium arsenite and sodium hydroxide (*Organic Syntheses*, Coll. Vol. I, 1941, p. 358). Other methods include the treatment of iodoform with iodine (Hofmann, *Annalen*, 1860, 115, 267), with sodium ethoxide (Butlerow, *Ann. Chim. Phys.* 1885, [iii], 53, 313), or with hydrogen iodide (Leben, *Z. Chem.* 1868, 712).

A 1:1 solution of phosphorus can be made in methylene iodide at ordinary temperatures.

**Methylene Diacetate**,  $\text{CH}_2(\text{OAc})_2$ .—A liquid, b.p. 169–171°, prepared from methylene iodide and silver acetate (Butlerow, *Annalen*, 1858, 107, 111), or, better, from paraformaldehyde, acetic anhydride, and a trace of concentrated sulphuric acid (Knoevenagel, *ibid.* 1914, 402, 127).

**Methylene Dibenzoate**,  $\text{CH}_2(\text{OBz})_2$ .—A crystalline solid, m.p. 99°, b.p. 225° with decomposition, prepared by heating paraformaldehyde and benzoyl chloride in the presence of zinc chloride (Descudé, *Compt. rend.* 1901, 133, 371).

**Methylene Diamine**,  $\text{CH}_2(\text{NH}_2)_2$ .—The free base is unstable, but can be prepared in solution from the stable crystalline dihydrochloride, which is made by condensing formamide with formaldehyde to give *methylene diormamide*,  $\text{CH}_2(\text{NH}\cdot\text{CHO})_2$  and then hydrolysing with hydrochloric acid:



Alkylated derivatives such as  $\text{CH}_2(\text{NR}_2)_2$ , where R is methyl, ethyl, or propyl, are known.

**Hexamethylenetetramine.** See FORM-ALDEHYDE, Vol. V, 320b.

B. A. K.

**METHYL ALCOHOL**,  $\text{CH}_3\cdot\text{OH}$ . Methanol, carbinol, hydroxymethane, wood naphtha (impure methyl alcohol).

B.p. 64.509°/760 mm.; variation of boiling-point with pressure  $dt/dp=0.0331^\circ\text{C./mm.}$  at  $p=760$  mm. (Wajciechowski, *J. Res. Nat. Bur. Stand.* 1936, 17, 721);  $\rho_{15}^{15}$  0.79647;  $\rho_4^{15}$  0.79577 (U.S. Bureau of Standards Tables Circ. No. 19, 1916, pp. 22–24); m.p.  $-97.8^\circ$ ;  $n_D^{14.5}$  1.33118; heat of vaporisation = 262.8 g.-cal./g. at  $15^\circ\text{C.}$ ; heat of combustion 170.9 kg.-cal./g.-mol.  $[\text{CH}_3\cdot\text{OH}(\text{liquid}) \xrightarrow{30} \text{CO}_2(\text{gas}) + 2\text{H}_2\text{O}(\text{liquid})]$  (Kharasch, *Bur. Stand. J. Res.* 1929, 2, 359); heat of formation 60.24 kg.-cal./g.-mol.

Methyl alcohol is a colourless, mobile, inflammable liquid of characteristic, pleasant odour when pure. It is miscible in all proportions with water. Methyl alcohol arises in the destructive dry distillation of wood, and is said to be present in small quantities in all fermented liquors. In the form of esters, such as oil of wintergreen (methyl salicylate), it is found in plants.

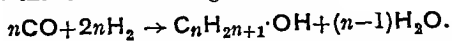
**Formation.**—Methyl alcohol may be produced from the dry distillation of wood, from the waste water of steamed wood pulp in paper manufacture, by the partial oxidation of methane, and by the catalytic reduction of oxides of carbon. Methyl alcohol also arises in many organic reactions by processes common to all aliphatic alcohols.

**Preparation.**—The principal method of manufacture of methanol was formerly through the dry distillation of wood. The rapid development of the synthetic process in the third decade of this century has considerably reduced the relative importance of this method, and at present probably less than one-tenth of the world's methanol output is derived from wood.

**Wood Distillation.**—The distillation of wood may be conducted in various ways according as the main object of the process is to produce charcoal, methyl alcohol, and other by-products or gas. The production of by-products is best carried out by the distillation of hardwood; softwood is used to a smaller extent, but yields only half the amount of methyl alcohol. The wood is introduced, either by stacking or by being run in on steel trolleys, into iron retorts, which are then heated to 400–500°C. by any suitable means. The gases resulting from the decomposition of the wood are passed into water-cooled condensers, and the liquor (crude pyroigneous liquor) is allowed to settle in wooden vats. The gases leaving the condenser may be scrubbed to recover methyl alcohol, acetone, etc. The settled tar is removed from the crude pyroigneous acid. The aqueous pyroigneous acid is distilled in order to remove "dissolved" tar; the original tar is steam distilled to recover methyl alcohol, etc., and the aqueous distillate added to the aqueous pyroigneous acid. Any oils which separate from the aqueous acid are water-washed and the washings returned to the aqueous acid.

of this reaction, which leads to difficulty of control and the possible damage of the converter, and to a wastage of compressed gas, by ensuring the absence of metals of the eighth group of the periodic table, which are known specifically to catalyse the methane reaction.

Another side reaction that may occur, again favoured by high temperatures, is that leading to the formation of higher alcohols:



The possibility of this reaction occurring can be reduced by the choice of a suitable catalyst.

The pressures and temperatures employed, together with the processes used for the manufacture of the synthesis gas, bear a great resemblance to the practice of the synthesis of ammonia, and it is, therefore, found that in most cases the manufacture of synthetic methyl alcohol is carried out by firms already versed in the technique of ammonia synthesis. In many cases synthetic methyl alcohol plants are run as an integral part of synthetic ammonia plants.

**History.**—Experimental work on the production of synthetic methyl alcohol dates from 1913, in which year the Badische Anilin und Soda-Fabrik concern carried out some experiments on the reduction of carbon monoxide under pressure. They succeeded in producing a mixture containing alcohols, acids, aldehydes, hydrocarbons, etc. This represented a new step, as previous attempts to reduce carbon monoxide had always led to the formation of methane. The B.A.S.F. discoveries were protected in G.P. 293787, 295202, and 295203. The First World War interrupted the experiments, which were, however, re-opened in 1922. The rapid success of these experiments led to a semi-technical plant being erected at the end of that year, followed by a full-scale plant at Leuna.

Independently of the German experiments, work had been carried out in France by Georges Patart, who patented a process for the production of alcohols by the reduction of oxides of carbon in 1921 (F.P. 540543). There have been conflicting claims to the prior invention of the synthetic process by the Badische and Patart companies (*see*, for instance, *Z. angew. Chem.* 1927, 40, 166; *Ind. Eng. Chem.* 1925, 17, 859). The Patart company did not operate its process, but issued licences for the manufacture of methyl alcohol according to its patents. The first methyl alcohol plants in France were erected in 1927–29. Other French pioneers were E. Audibert and Georges Claude, who each worked out individual processes.

The development of the synthetic methyl alcohol industry in the rest of the world was rapid. The import of cheap German methyl alcohol upon the U.S. market instigated intensive research by E.I. Du Pont de Nemours, which led to the speedy erection of plants. Plants were also erected in England, Belgium, and Holland. More recently Italy and Japan have entered the field; an individual process has been developed by G. Natta in the former country. The U.S.S.R. has carried out original research which, in conjunction with plants operated under licence, has enabled her to meet part of her large demand for formaldehyde.

Any estimate of the World production of synthetic methyl alcohol must be to a large extent speculative, as full statistics are not available. However, it is probable that the total World production of methyl alcohol was of the order of 300,000 tons per annum immediately preceding the Second World War. Of this total, probably less than one-tenth was produced by wood distillation.

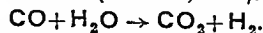
#### THE SYNTHETIC METHYL ALCOHOL PROCESS.

The process consists of the following steps:

- (a) The production of a mixture of carbon monoxide and hydrogen (or carbon dioxide and hydrogen) of a suitable composition.
- (b) and (c) Purification and compression of the gas mixture.
- (d) Heating the gas to reaction temperature by means of external heaters, or heat interchangers, or both.
- (e) Passage of the heated gas over the catalyst.
- (f) Separation of the methyl alcohol and passage of unreacted gas, either back to the converter or to some other process.
- (g) Purification of the crude methanol by distillation.

(a) **Production of Synthesis Gas.**—The methods of preparation of the synthesis gas vary according to the sources of carbon and hydrogen available, and different methods are preferred by different manufacturers. It is not usual to use a synthesis gas containing the stoichiometric proportions of carbon monoxide and hydrogen, but rather one containing an excess of hydrogen. The exception to this practice occurs when a self-contained circulation system is used, in which case the gas fed to this system to compensate for the formation of methyl alcohol must be of the stoichiometric composition if the composition of the gas in the circulating system is to remain unchanged. The following are the main general methods used:

1. **Water Gas.**—The gas formed by the reaction  $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$  contains the desired components, but not in the correct proportions, as it has been pointed out that the ratio of hydrogen to carbon monoxide should be at least 2 to 1. Water gas may, however, be treated with steam over a promoted iron catalyst at an elevated temperature in order to increase the proportion of hydrogen at the expense of that of carbon monoxide (*v. Vol. I*, 334c).



If this reaction is controlled so that it proceeds to any given extent, and the resultant carbon dioxide is removed by water-washing under pressure, or by other suitable means, a synthesis gas of any composition between that of water gas and nearly pure hydrogen may be obtained.

If, instead of steam, a mixture of steam and air is used as the gasifying agent, a gas containing nitrogen is formed, which after being used for methanol synthesis, followed by removal of

**Zinc-Chromium Catalysts.**—This, the most important class of catalysts, includes the original catalysts of Patart, which consisted of basic zinc chromate reduced in the synthesis gas (B.P. 247178, 1925; 247932, 1925). The addition of a heat-conducting material is also claimed by Patart to improve such a catalyst by preventing local over-heating (F.P. 618439, 1926). A zinc chromite of the composition  $4\text{ZnO} \cdot \text{CrO}_3$  has also been patented by I.C.I. (B.P. 275345, 1926). E.I. Du Pont de Nemours (B.P. 272555, 1926) claim a catalyst made by heating a chromate of zinc either alone or with other metals at a temperature above  $600^\circ$ , also a catalyst formed by ignition of a basic zinc ammonium chromate (B.P. 313093, 1928). A methyl-alcohol catalyst can also be made by mechanical admixture of zinc and chromium oxides either alone (Doglov and Karpov, Amer. Chem. Abstr. 1934, 28, 5212) or with chromic acid (Veltistova, Doglov and Karpov, *ibid.* 1935, 29, 1059) or with the addition of zinc chloride (Commercial Solvents Corporation, B.P. 272864, 1926; U.S.P. 1625925; F.P. 644525), or by ignition of the mixed oxides in the presence of ammonium nitrate (Commercial Solvents Corporation, U.S.P. 1668838, 1928). Zinc oxide may be dissolved in molten potassium dichromate, and the solidified mass broken up and used as a methyl-alcohol catalyst (I.G. Farbenind. A.-G., B.P. 229714, 1923), or zinc oxide may be treated with chromic acid, as claimed by I.G. Farbenind. A.-G., in B.P. 286284, 1927, in which zinc oxide is made into a paste with magnesium chloride solution, the paste heated to expel acid, and the product then heated in a stream of air carrying chromic acid. The magnesium chloride adds to the mechanical strength of the catalyst.

Active catalysts may be prepared by heating the basic carbonates of zinc and chromium either alone (I.C.I. Ltd., B.P. 293056, 1926), or with zinc chromate or basic zinc chromate (I.C.I. Ltd., B.P. 290399, 1926). The Compagnie des Mines de Béthune have claimed catalysts formed by impregnating a porous support with the formates of zinc and chromium either alone (B.P. 274492, 1926) or with the addition of nickel or nickel oxide or formate (B.P. 275600, 1926).

Zinc-chromium catalysts are also mentioned in the following patents: B.A.S.F., B.P. 229715, 1923; Commercial Solvents Corporation, U.S.P. 1797569, 1931; British Celanese, B.P. 345649, 1929 (by electrolysis of a solution of the nitrates or formates); E.I. Du Pont de Nemours, U.S.P. 1984884.

A catalyst formed by the admixture of zinc sulphide and chromium oxide has been claimed (British Celanese, B.P. 334924, 1929). The insensitiveness of an ordinary zinc-chromium catalyst makes it suitable for use in a "guard" converter before a converter containing a sulphur-sensitive catalyst (Dreyfus, B.P. 335962, 1929).

There is rough agreement among inventors as to the ideal proportion of zinc to chromium. Patart, the originator of the zinc-chromium catalyst, states (B.P. 252361, 1925) that for a zinc oxide-chromium trioxide catalyst, the molar proportion of zinc oxide to chromium

trioxide should be at least 2:1 (1:1 atomic ratio). In the case of a zinc chromate the atomic ratio should be at least 1.5:1. I.C.I. Ltd. (B.P. 275345) claim a zinc chromate of atomic ratio 4:1. It is stated by B.A.S.F. (B.P. 227147) that zinc oxide containing only 1% of  $\text{Cr}_2\text{O}_3$  is an excellent catalyst. Veltistova, Doglov, and Karpov (*l.c.*) obtain satisfactory results with a zinc-chromium trioxide-chromic acid catalyst, which has a zinc-chromium atomic ratio of 8:3. A 2:1 catalyst is claimed by Doglov and Karpov (*l.c.*). Ivanov and Gusev (Amer. Chem. Abstr. 1936, 30, 1525) state that an 8:3 catalyst is the most efficient at  $370^\circ$ ; and Nikitin (*ibid.*, p. 2170) finds that catalysts containing more chromium than 8:2.4 lead to the increased formation of by-products.

The position has been reviewed by Molstead and Dodge (Ind. Eng. Chem. 1935, 27, 134), and it was found that in the case of catalysts formed from solutions of the mixed nitrates by ammonia precipitation, the highest initial activity is given by a catalyst of atomic ratio 3. Catalysts with more chromium have a lower initial activity, but increase in activity during tests, the improvement being accelerated by the use of temperatures higher than the running temperature. For long service, the best catalyst is found to be one of atomic ratio 1.

It has been shown that maximum adsorption of carbon monoxide takes place on catalysts of atomic ratio 4, and the maximum hydrogen adsorption at 1.5. Maximum activity towards decomposition occurs at approximately 2, and this coincides with maximum activity to synthesis. It is suggested that maximum reaction takes place when equal numbers of hydrogen and carbon monoxide molecules are adsorbed on the catalyst.

**Zinc-Chromium-Alkali.**—The addition of a compound of an alkali metal to a zinc-chromium catalyst tends to lead to the formation of higher alcohols than methanol, in addition to methanol itself. *E.g.*, I.C.I. Ltd. (B.P. 293056, 1926) claim that the addition of alkali to a zinc-chromium catalyst obtained by heating together basic zinc and chromium carbonates makes the catalyst suitable for higher-alcohol production. I.G. Farbenindustrie A.-G. (B.P. 286284, 1927) achieve the same result by the addition of an alkali bichromate to a zinc-chromium catalyst.

**Zinc.**—The most important member of this class is the smithsonite catalyst of Natta. Smithsonite is a natural zinc carbonate, which after being broken down and heated, is suitable without further treatment as a methyl-alcohol catalyst. Natta has stated (B.P. 330919, 1929), however, that the superiority of smithsonite over artificially prepared zinc carbonates is probably due to the impurities present in the mineral, which act as promoters. Natta has also described the preparation of methanol catalysts by the decomposition of organic salts of zinc, for instance, zinc acetate (Amer. Chem. Abstr. 1938, 32, 5166). British Celanese Ltd. (B.P. 300142, 1927) claimed a catalyst made by heating a zinc carbonate gel; I.C.I. Ltd. (B.P. 316113, 1928) describe a catalyst made by heating zinc carbonate alone. The use of zinc oxide alone has been patented by Dreyfus



synthesis system in those plants where the methyl-alcohol plant is run in conjunction with ammonia synthesis.

The circulators used in a circulating system resemble closely the similar machines used in ammonia-synthesis systems. A device is used in the Casale system whereby the passage of make-up gas to the circulating system is used to induce circulation on the principle of a steam injector.

(g) Distillation.—Crude synthetic methyl alcohol is usually contaminated with water, the amount of which depends on the extent to which water-forming reactions are allowed to take place. The principal water-forming reactions are those which involve the reduction of carbon dioxide, and the formation of methane, dimethyl ether, or higher alcohols. In addition to water, the crude product may be contaminated with small amounts of amines (if nitrogen is present in the synthesis gas), higher alcohols, aldehydes, hydrocarbons, sulphur compounds, and iron carbonyl. It is essential that the last two impurities be removed if the methyl alcohol is to be used for the production of formaldehyde by catalytic oxidation over a silver catalyst.

The production of methyl alcohol of A.R. quality can be accomplished without much difficulty by the use of ordinary distillation technique. The iron carbonyl may be first removed by air oxidation, which precipitates the iron as a hydrated oxide, and the iron-free crude methyl alcohol submitted to distillation on a continuous column, from which water and higher alcohols are removed as a purge, and aldehydes, hydrocarbons, and other light ends removed as a top product, together with some methyl alcohol. Nearly pure methyl alcohol is removed from a point near the top of the column.

#### ANALYSIS.

Detection.—No simple specific test applicable to the detection of methyl alcohol under all conditions is known. Tests should, therefore, be applied taking into account the other known constituents of the mixture, and more than one independent method should be used in order to confirm the presence of methyl alcohol.

Most tests depend on the production of formaldehyde by oxidation of the methyl alcohol. This is best carried out by a regulated oxidation procedure, such as that of Denigès (Compt. rend. 1910, 150, 832). The oxidising medium is potassium permanganate and sulphuric acid, and the formaldehyde is detected by the coloration produced by Schiff's reagent. This test is capable of being made quantitative by careful control of the conditions, and by comparing the colour produced with that arising from known amounts of methyl alcohol. This test has been modified for use in the U.S. Pharmacopœia, which should be consulted for details. The Denigès test will detect about 0.2% of methyl alcohol (expressed as a fraction of total alcohols present) and the U.S. Pharmacopœia test about 0.3%.

Chapin (J. Ind. Eng. Chem. 1921, 13, 543) has modified the Denigès test by the introduction of phosphoric acid in the place of sulphuric acid, and the use of a standard Schiff's solution pre-

pared according to the method of Elvove (*ibid.* 1917, 9, 295).

The Vousek test (J.S.C.I. 1900, 28, 823) uses chromium trioxide as the oxidising agent, and the formaldehyde is detected by the blue colour produced in the presence of an alcoholic solution of gallic acid. Alternatively, the use of morphine sulphate or apomorphine has been proposed as a colour test for the formaldehyde. Crystalline derivatives of formaldehyde may be used as means of detection, such as that with  $\beta$ -naphthol (E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. I, New York, 1941, p. 24), or the compound formed between hexamethylenetetramine, obtained by the action of ammonia on the formaldehyde, and mercuric chloride.

The Vivario test (J. Pharm. Chem. 1915, 10, 145) depends on the oxidation of methyl alcohol to formaldehyde by hydroxylamine, followed by the formation of formaldoxime with excess hydroxylamine. Formaldoxime on heating gives hydrocyanic acid, which may be readily detected.

The Riche-Bardy method (Compt. rend. 1875, 80, 1076) depends on the production of Methyl-aniline Violet from the methyl alcohol. The alcohol sample is converted into methyl and ethyl iodide, which are separated and treated with aniline. The product is oxidised, and the dye extracted with alcohol. Ethyl alcohol alone gives a red dye, but the presence of methyl alcohol causes a violet tint to appear. Pieces of wool or silk floss may be dyed and compared with standard samples resulting from known mixtures of methyl and ethyl alcohols.

For a rapid microchemical test, see Vol. V, 302a.

Estimation of Methyl Alcohol.—Although the above methods of detecting methyl alcohol in the presence of ethyl alcohol may be made roughly quantitative by comparison of the effects produced with those caused by known amounts of methyl alcohol, more accurate quantitative methods are available.

Krell's method (Ber. 1873, 6, 1310) has been used in the British Government Laboratory for the estimation of methyl alcohol in wood naphtha. It involves the conversion of the methyl alcohol into methyl iodide, which is distilled off and measured. All compounds containing alkoxy-groups are converted to iodides by this method, so that the process cannot be used in the presence of esters or other alcohols.

The estimation of methyl alcohol in formaldehyde solutions is of commercial importance. This may be carried out by conversion of the formaldehyde into a non-volatile compound, distilling off the methyl alcohol, and estimating this separately. Suitable reagents for combination with the formaldehyde are sodium bisulphite (Bamberger, Z. anorg. Chem. 1904, 17, 1246) or sodium phenylhydrazinesulphonate, and many others. A suitable procedure is described by Gnehm and Kaufler (Z. angew. Chem. 1904, 17, 673). Alternatively, the formaldehyde may be determined initially, for instance, by the hydroxylamine method (Brochet and Cambier, Compt. rend. 1895, 120, 449), and the mixture oxidised with chromic acid, the amount consumed being measured. The contri-

**METHYL ORANGE**, *Helianthin*, *Tropæolin D* (v. Vol. II, 640*d*; VI, 426*a*). In acid solution Methyl Orange is bleached by free chlorine but not by chloramines, and may be used as a distinguishing test, e.g., in a treated water-supply (Besemann, Amer. Chem. Abstr. 1929, 23, 792).

J. N. G.

**METHYL RED** (v. Vol. II, 641*a*) is frequently used instead of Methyl Orange, especially for titrating ammonia (Tizard, J.C.S. 1910, 97, 2489; Howard and Pope, *ibid.* 1911, 99, 1333; Lehmann and Wolff, *ibid.* 1917, 112, ii, 326).

J. N. G.

**METHYL VIOLET**, *Methyl Violet 2B*, a triphenylmethane dyestuff consisting chiefly of a mixture of the hydrochlorides of tetra-, penta-, and hexa-methylparosanilines. Green powder with a metallic lustre. It dyes violet shades on wool, silk, and mordanted cotton, and is used in the manufacture of inks. Methyl Violet has a limited application as an indicator for detecting strong acids in the presence of weak acids, the following colours being shown: pH -0.3, yellow; 0, yellow-green; 1, green-blue; 2, blue-violet; 3-13, violet fades (E. B. R. Prideaux, "Theory and Use of Indicators," London, 1917, p. 349).

Methyl Violet is an antiseptic, but for clinical purposes Crystal Violet is generally employed.

J. N. G.

"**METHYLANOL**" (v. Vol. VI, 226*a*).

## METHYLANTHRACENE AND OTHER SUBSTITUTED ANTHRACENES.

### CONTENTS.

Structure (p. 20*c*).

*meso*Alkylanthracenes; Preparative Methods. Review of methods (p. 22*a*).

- Addition of alkyl (aryl) groups to anthracene and its derivatives (p. 22*c*).
- Addition of substituent groups prior to formation of anthracene ring (p. 31*c*).
- Simultaneous introduction of alkyl (aryl) groups and anthracene ring-closure (p. 33*d*).

Transannular tautomerism of 9-alkylanthracenes (p. 35*a*).

*Bz*-Methylanthracenes (p. 45*b*).

Anthracene Carboxylic Acids (p. 52*a*).

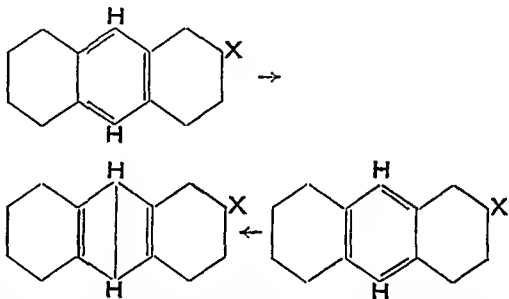
Dianthracenes (p. 52*c*).

Alkylanthracene Derivatives found in Nature (p. 52*d*).

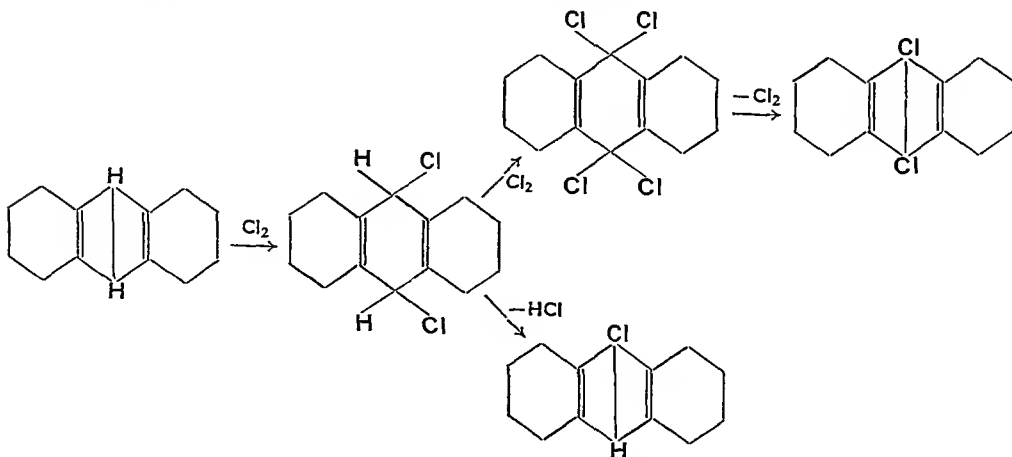
Literature References (p. 52*d*).

### STRUCTURE.

The structural formula of anthracene has two similar benzene rings connected through a dissimilar central ring, on the properties of which the chemical behaviour and isomerism of the anthracene derivatives largely depend (*cf.* ANTHRACENE, Vol. I, 382). The central ring in anthracene can be regarded either as *o*-quinonoid, or as being *p*-quinonoid but possessing a bridge bond which is opened by addition or oxidation. The latter view is scarcely tenable on modern knowledge of strain, but is valuable in offering a simple mechanism for the reactions of anthracene derivatives by addition, which opens the bridge bond. In the present article its use is largely retained on this ground; it must however, be understood that it is conceived as being merely a device to indicate the mean position of equilibrium between the two *o*-quinoid forms which are possible, for instance in a monosubstituted derivative:



In simple reactions of anthracene, for instance halogenation, the bridge bond is like an ethylenic double bond. Addition occurs, and then substitution, and either halogen or halogen acid can be abstracted, the di- or mono-halogen anthracene being formed, with re-formation of the bridge:



Generally, derivatives having the bridge bond or *o*-quinonoid structure are fluorescent in solution; those having the *p*-quinonoid are not.

The central ring, in acquiring two oxygen atoms by oxidation, can give rise to several distinct stages between 9:10-dihydroanthracene

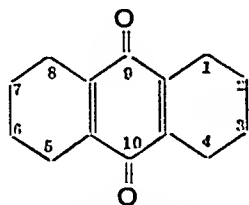


and 9:10-dioxoanthracene or anthraquinone. Four successive stages of oxidation can be observed in practice, but at each of the two middle stages pairs of tautomeric forms are obtained where one member has the *o*-quinonoid and the other the *p*-quinonoid central ring. In addition, the dihydro-derivatives of the mono- and di-hydroxyanthracenes make up in all nine types of compound between dihydroanthracene and anthraquinone inclusive:

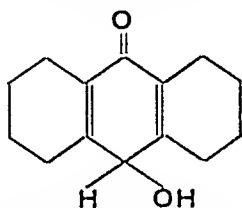
*p*-Quinonoid.

*o*-Quinonoid or Bridge Bond.

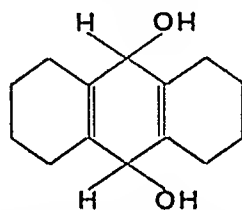
Reduction.



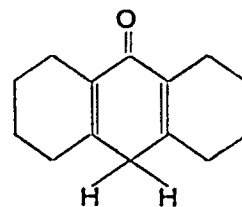
9:10-Dioxoanthracene (Anthraquinone).\*



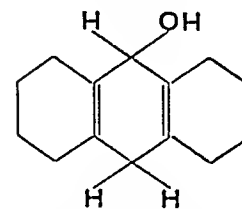
9-Oxo-10-hydroxy-10-hydroanthracene (10-Hydroxyanthrone, 9-Oxanthrone).



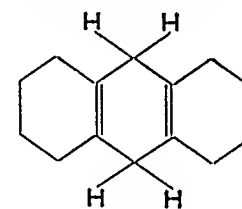
9:10-Dihydroxy-9:10-dihydroanthracene (Dihydroanthrahydroquinone).



9-Oxo-10-hydroanthracene (Anthrone).

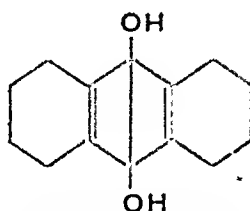


9-Hydroxy-9:10-dihydroanthracene (Dihydroanthranol-9).



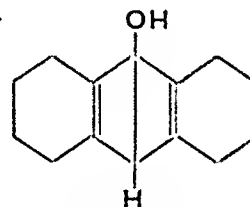
9:10-Dihydroanthracene.

$\rightleftharpoons$



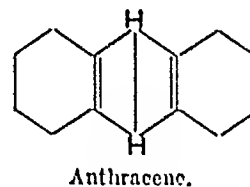
9:10-Dihydroxyanthracene (Anthrahydroquinone).

$\rightleftharpoons$



9-Hydroxyanthracene (Anthranol-9).

$\xrightarrow{-H_2O}$



Anthracene.

Oxidation.

\* NOTE.—Throughout the present memoir, anthrones and anthranols are numbered with the oxygen in the 9-position, anthraquinone being numbered in the accepted manner shown above. Alternative names used in the literature are given in parentheses.

The series of anthracene derivatives obtained by substituting the central-ring hydrogens by alkyl or aryl groups, or the *meso*- or 9-mono-, or 9:10-dialkyl-anthracenes, have properties distinct from those in which the hydrogens of the external benzene rings are similarly substituted (*Bz*-derivatives). For any one alkyl group in a *meso*-position in anthracene there is one mono- and one di-substituted derivative, while for the *Bz*-derivatives there are two mono-, twelve di-, fourteen tri-, and sixteen tetra-substituted derivatives possible. Where both *meso*- and *Bz*-positions are substituted, larger numbers of isomers are possible.

The *meso*-alkyl derivatives are the most thoroughly studied and are therefore discussed first.

### *meso*ALKYLANTHRACENES.

The principal methods by which the *ms*-alkyl and -aryl anthracenes may be prepared are as follows:

A. Where the substituent group is added to a preformed anthracene ring.

1. C-alkylation of reduction products of anthraquinone.
2. Action of Grignard reagents on anthrones and anthraquinones. Preparation of anthrones, and their properties.
3. By Friedel-Crafts type reactions:
  - (a) with anthracene and alkyl halides,
  - (b) with anthracene and acid halides (or anhydrides),

- (c) from halogeno-anthracenes and reactive aryl compounds,
- (d) with halogeno-anthrones and aromatic compounds.

4. The reactions of anthrones with aldehydes and unsaturated compounds.

B. The substituent groups are added prior to forming the anthracene ring.

1. From alkyl (aryl) benzylbenzoic acids.
2. By reaction of Grignard reagents on phthalides.
3. Miscellaneous methods.

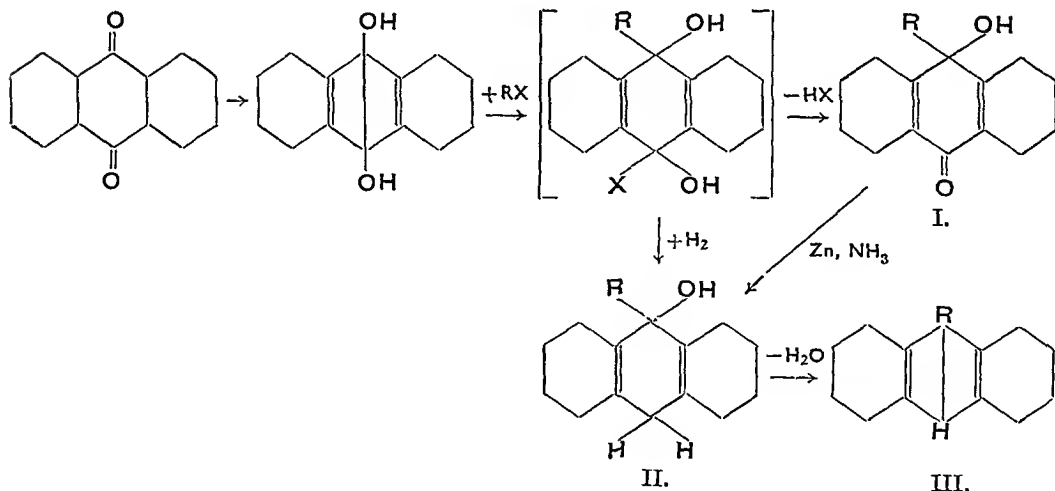
C. Simultaneous introduction of substituent groups, and anthracene ring closure.

(These methods will be discussed in turn.)

### A. ADDITION OF ALKYL (ARYL) GROUPS TO ANTHRAQONE AND ITS DERIVATIVES.

1. C-alkylation of Reduction Products of Anthraquinone.—Liebermann and his school studied extensively the reaction which occurs when anthraquinone is reduced with zinc dust and caustic alkali, and an alkyl halide of at least two carbon atoms added.<sup>17, 18, 23, 64</sup>

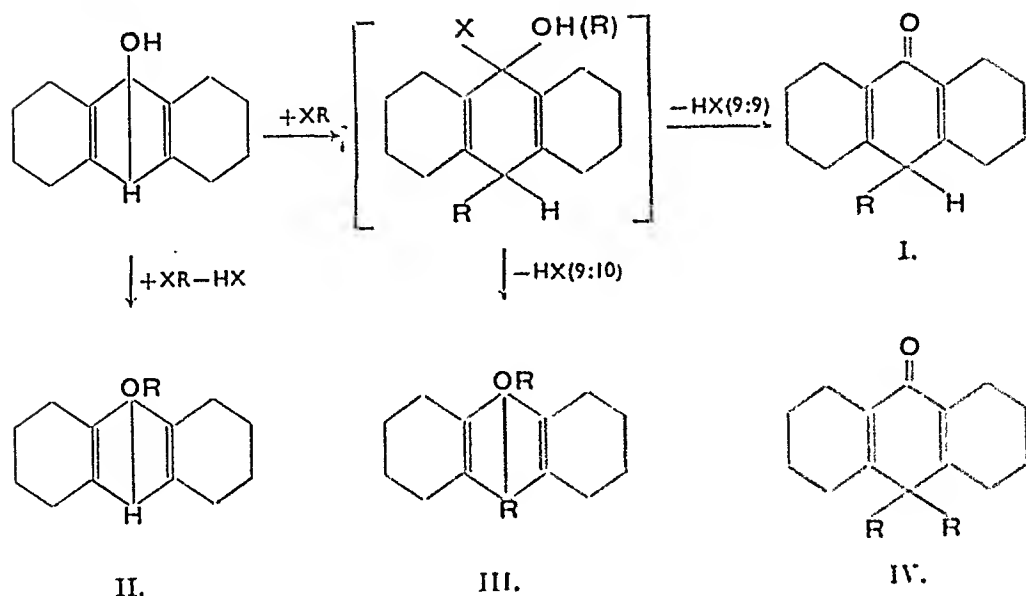
The first compounds formed by adding alkyl halide to the reduced alkaline solution are the 10-alkyl-10-hydroxy anthrones (I); under more vigorous conditions, however, further reduction takes place with formation of 10-hydroxy-10-alkyl-9:10-dihydroanthracenes (II), which easily lose water from the 9:10-positions to form mono-alkylantracenes (III).



The (I) series are also obtained by the Grignard method (v. p. 236) from anthraquinone, by keeping the latter in excess. The hydroxyl is readily replaced by chlorine by means of phosphorus pentachloride. They are readily reduced by zinc and ammonia to (II), while more vigorous reduction yields 9-alkyl-9:10-dihydroanthracenes. When  $R$ =allyl in (I), it is noteworthy that sodium amalgam preferentially reduces the double bond<sup>152</sup> giving 10-*n*-propyl-10-hydroxy-

anthrone. 9-Methylantracene is not available by this route, as the main product with methyl halides is anthranol methyl ether.

Anthrones, when boiled with caustic potash and alkyl (aryl) halides react vigorously in the anthranol form and are alkylated<sup>60, 61</sup> to the 10-alkyl(aryl)anthrones, but can also react further, both to introduce a second group directly attached to carbon and to etherify the hydroxyl group, so that four products are possible:



While (II) is of rarer occurrence, (I), (III), and (IV) are plentifully observed, as the table below shows.

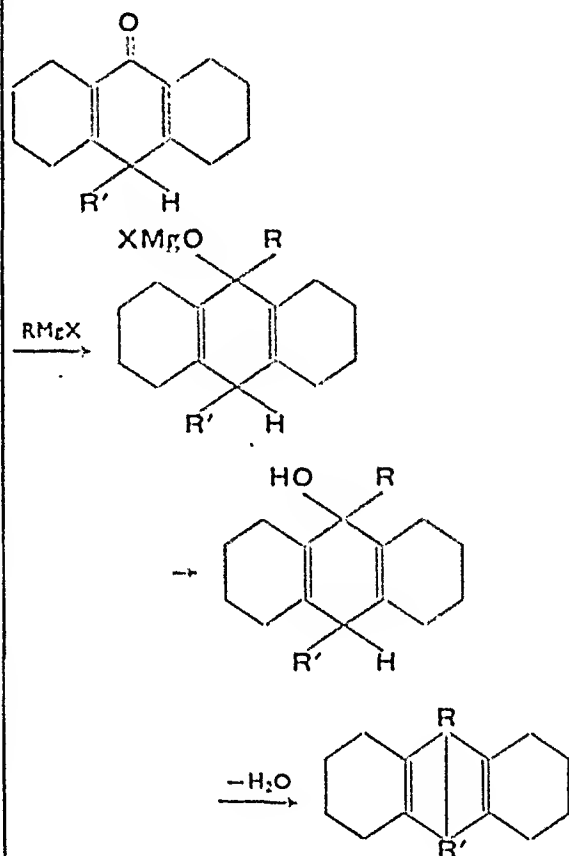
Alkyl group.	Product.	Reference.
Methyl . . .	(III), (IV). (I).	61, 193, 207, 215 215, 2525
Ethyl . . .	(II), (III), (IV).	60, 193
<i>n</i> -Propyl . .	(III), (IV).	61
<i>iso</i> Amyl . .	(I).	61
Benzyl. . .	(IV).	61, 204, 219, 252c, 259, 277 219, 252a, 252b, 274, 275
	(I).	

The monoalkylanthrones may be reduced to 9-alkylanthracenes, and the dialkylanthrones to 9:9-dialkyl-9:10-dihydroanthracenes, but the first-mentioned series can also be used to produce unsymmetrical 9:10-dialkylanthracenes by method A2, next discussed.

**2. Action of Grignard Reagents on Anthrones and Anthraquinones.**—Here the major reaction is normal in each case, one or both carbonyl groups, as the case may be, being converted to alkyl-carbinol groups in the usual way. Thus anthrones yield 9-hydroxy-9-alkyl-9:10-dihydroanthracenes, and 10-alkylanthrones yield 9-hydroxy-9:10-dialkyl-9:10-dihydroanthracenes. Both can be dehydrated, usually in acetic acid solution by means of a little added hydrochloric or sulphuric acid, yielding 9-alkyl- or 9:10-dialkyl-anthracenes; the alkyl groups can also be the same or different.<sup>125, 153, 161, 161, 200, 201, 202, 228a, 228c, 232, 238, 241, 245, 249, 251, 252, 253a, 253c, 256a, 258a, 259a, 266, 207, 272, 277, 300</sup>

The reaction is, however, complicated by the enolising effect of the Grignard reagent, and the anthranol so formed gives a magnesium-organic complex which only regenerates anthranol with acid. It is usual to employ 2½–3 molecules of the Grignard reagent to minimise this effect, but it is worthy of note that the enolising tendency is much diminished when lithium phenyl is employed as the reagent.<sup>301</sup>

Generally, good yields are confined to a few reagents, such as methyl iodide, ethyl bromide, benzyl chloride, and bromobenzene. The last generally gives good results; thus 10-phenyl-anthrone with phenyl magnesium bromide



followed by dehydration gives a 66% yield of 9:10-diphenylanthracene. Methyl magnesium iodide or ethyl magnesium bromide and 1:5-dichloroanthrone yield, after dehydration, a 75% yield of 1:5-dichloro-9-methyl- or -ethyl-anthracene.<sup>232</sup> Although the 1:5-dichloro-9-

hydroxy-9-alkyl:9:10-dihydroanthracenes are stable enough to be recrystallised from acetic acid or alcohol and do not lose water on keeping in a vacuum desiccator, yet when dissolved in acetic acid it is only necessary to add a few drops of mineral acid to cause the immediate formation and crystallisation of 1:5-dichloro-9-alkylanthracenes.

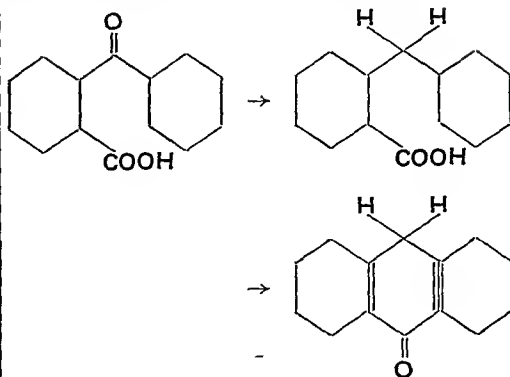
Owing to the mechanism of this final dehydration, which consists in the loss of the elements of water across the 9:10-positions, if alkoxy- or acyloxy-groups are already present in the 10-position of the anthrones, then the alcohol or acid may be split off in the final step. This usually consists of the treatment with hydrochloric acid in acetic acid solution; the methoxy-group may then be replaced even by chlorine. Thus 10-methoxyanthrone with benzyl magnesium chloride gives a 9-hydroxy-10-methoxy-9:10-dihydroanthracene which loses methyl alcohol to give 10-chloro-9-benzylanthracene.<sup>272</sup> Again, 10-acetoxy- (or benzyloxy-)anthrone-9 and its *Bz*-methyl derivatives, with methyl magnesium bromide followed by the dehydrating reagent, split off acetic (or benzoic) acid to give 9:10-dimethylanthracenes.<sup>300</sup>

Cases where the dialkyl-dihydroanthranols do not yield anthracenes but alkyl-alkylidene-dihydroanthracenes, owing to co-ordination effects of the  $\alpha$ -chlorines present are discussed later in this memoir.<sup>252b</sup>

The enolisation which reduces the yield with Grignard reactions from anthrones can no longer occur when 10:10-dialkyl(aryl)anthrones are employed as starting materials, hence good yields are obtained, but the products are 9-hydroxy-9:10:10-trialkyl(aryl)-9:10-dihydroanthracenes which cannot be dehydrated, but only reduced to the corresponding 9:10:10-trialkyl(aryl)anthracenes.<sup>200</sup> One of the 10:10-substituents may be a hydroxy- or methoxy-group; the latter gives good results.<sup>115, 116</sup>

*The Preparation of Substituted Anthrones* (cf. ANTHRONE, Vol. I, 430).—The preparation of anthrones containing substituents is an essential step in building up a wide variety of *ms*-alkylanthracenes, and it is convenient to discuss the subject at this point. As anthrone and anthranol are unsymmetrical anthracene compounds, one substituent in the *Bz*-rings of anthracene can give rise to two isomers; in the case of two substituents in the *Bz*-rings, when these are symmetrical, only one anthrone can exist, but when unsymmetrical there are again two isomers.

Anthrone was first produced by reduction of anthraquinone by means of hydriodic acid<sup>23</sup> and, later, more economically by tin and hydrochloric acid<sup>54</sup> or reduction under pressure with caustic potash and carbohydrates,<sup>195</sup> at low temperatures with aluminium and sulphuric acid,<sup>134</sup> or by means of alkaline hydrosulphites.<sup>209</sup> More recently catalytic reduction of anthraquinone by hydrogen and nickel has been stated to give good results.<sup>222</sup> Anthracene can be oxidised to dihydrodianthrone with acetic and nitric acids and the product reduced to anthrone.<sup>204</sup> There is also the method of reducing *o*-benzoylbenzoic acid by activated zinc and ammonia to *o*-benzylbenzoic acid, followed by ring-closure with sulphuric acid to anthrone,<sup>76, 240</sup>



which in a number of cases is useful for confirming constitution, as the 2'- and 4'-mono-substituted acids can only give single compounds when ring-closed, whereas the 3'- and 5'-derivatives can each give mixture of two isomers. Similar rules apply when two substituents are present.

*Properties of Anthrones.*—The *Bz*-substituted anthrones have been prepared as pure single isomers by a variety of methods, largely by the work of the late A. G. Perkin and his collaborators for hydroxyanthrones,<sup>269</sup> who found the method of boiling hydroxy- and alkoxy-anthraquinones with stannous chloride and concentrated hydrochloric acid very useful, while E. de Barry Barnett and his school chiefly investigated, and in great measure cleared up, various inaccuracies in the polychloro- and polymethyl-anthrones by various methods, such as the reduction and ring closure of *o*-benzoylbenzoic acids<sup>240, 251, 265, 267, 270, 277</sup> by tin and hydrochloric acid,<sup>204, 205, 251, 257, 259</sup> aluminium powder and sulphuric acid,<sup>205, 251, 252a, 267, 274</sup> zinc and acetic acid,<sup>252a, 255a, 266a</sup> or stannous chloride and hydrochloric acid.<sup>258, 275</sup> Steyermark prepared *Bz*-1-hydroxy-*Bz*-methylanthrones,<sup>261</sup> and Zahn a further series of *Bz*-hydroxy-methoxy- and -hydroxy-acetoxyanthrones.<sup>278, 285</sup>

The development of the chemistry of anthrone and anthranol was slow until K. H. Meyer<sup>155</sup> showed that Liebermann's anthrone was a mixture of the two tautomers, and first prepared anthranol in a state of purity by acidifying the alkaline solution at low temperature. It passes readily into anthrone even on keeping, while anthrone is stable, and anthranol is at once oxidised in solution, even by atmospheric oxygen, to dihydro-dianthrone. The many doubts that existed previously owing to the varying behaviour of anthrone-anthranol mixtures under different conditions was largely cleared up by the work of K. H. Meyer, whose methods enabled the composition of the equilibrium between the tautomers in any solvent to be determined. Thus the velocity of attaining equilibrium is in descending order in the solvents acetone, ether, chloroform, acetic acid, alcohol, benzene, and light petroleum. The equilibrium usually favours anthrone, but in acetic acid is in favour of anthranol. Solvents in which-only anthranols can exist are pyridine and piperidine.

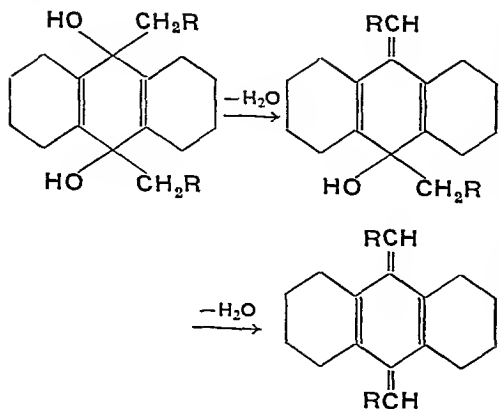
The chemical behaviour of anthrone and

anthrone, and acetic acid 10-acetoxyanthrone. Ammonia and amines convert 10-bromoanthrone to dianthrones,<sup>174</sup> but primary arylamines yield 10-arylaminoanthrones by condensing in the *p*-position to the nitrogen. However, *Bz*- and *ms*-substituents exert a very powerful influence on this reaction, and even a *Bz*-2- or -3-methyl group enables 10-arylamino-derivatives to be obtained with primary, secondary, or tertiary amines.<sup>199, 266b, 270</sup>

Bromoanthrone also reacts readily with resorcinol, with no condensing agent, to give the dihydroxyphenyl-derivative.

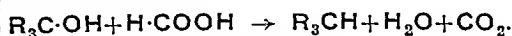
Anthraquinones, with alkyl (aryl) magnesium halides, can give the hydroxyalkylanthrones, but they generally yield 9:10-dihydroxy-9:10-dialkyl - 9:10 - dihydroanthracenes (dialkyl-anthradiols),<sup>110, 116a, 153, 161, 190, 201</sup> which can be easily reduced to the dialkylanthracenes, as they are strong oxidising agents. Variable yields have been reported, but for instance 2-methylanthraquinone gives with phenyl magnesium bromide a 95% yield of 9:10-diphenyl-2-methylanthradiol.<sup>116a</sup> Barnett only obtained a 50% yield of 9:10-diphenylanthradiol from anthraquinone,<sup>241</sup> some anthrahydroquinone being formed by the reducing action of the Grignard reagent, which is a frequent source of loss. It may even be made to lead direct to the anthracene derivative, for 1-chloroanthraquinone when boiled with 4 mol. of phenyl magnesium bromide yields 1-chloro-9:10-diphenylanthracene, only traces of the diol being observed.<sup>241</sup> Good yields have been obtained from several mono- and di-alkylanthraquinones and phenyl magnesium bromide, *n*-butyl ether being used as solvent.<sup>294</sup> An interesting special case occurs when 10-acetoxy-2-methylanthrone is treated with magnesium methyl bromide, which causes some replacement of the 10-acetoxy-group by methyl, in addition to the normal carbinol formation on the 9-carbon atom, so yielding directly a significant amount of 2:9:10-trimethylanthracene.<sup>300</sup>

The dialkylanthradiols have a tendency to lose water from a 9 or 10 position and the  $\alpha$ -carbon of the alkyl group in the same position.



The dialkylanthradiols liberate iodine from potassium iodide and acetic acid, and are readily reduced to the dialkylanthracenes by zinc dust

and acetic acid, by hydriodic acid and phosphorus,<sup>16, 23</sup> or preferably with glacial formic acid, with or without sodium formate,<sup>190</sup> as this is a quantitative method for all triaryl-carbinols:



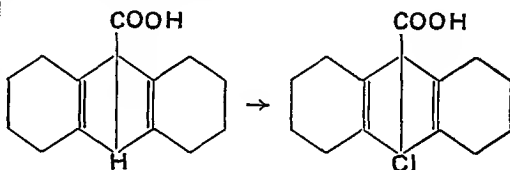
It is, however, of interest to note that 1:2:9:10-tetramethyl - 9:10 - dihydroanthraquinone - diol does not give the tetramethylanthracene on reduction with hydriodic acid, but the reduction proceeds to the limiting stage, the corresponding dihydroanthracene.<sup>299</sup>

If the anthraquinone is kept in excess, only one carbonyl group reacts and the 10-hydroxy-10-alkylanthrones are formed exclusively.

### 3. By Friedel-Crafts Type Reactions.

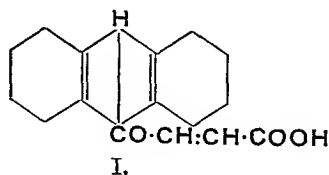
(a) *Between Anthracene and Alkyl Halides.*—This reaction is of little importance. The only recorded examples are the condensation with cyanogen bromide and aluminium chloride to give anthranyl cyanide,<sup>194</sup> and with benzyl chloride and zinc dust to give 9:10-dibenzylanthracene.<sup>91, 97</sup>

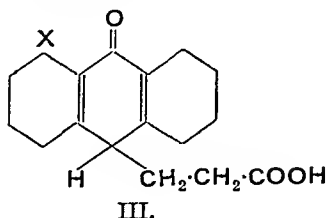
(b) *Anthracene and Acyl Halides, Anhydrides.*—Liebermann and his pupils obtained small yields of anthroic acid from anthracene and phosgene, or at higher temperatures, 10-chloroanthroic acid,<sup>1, 2, 41</sup> or from 9-chloroanthracene and phosgene.<sup>58</sup>



Better yields are obtained with oxalyl chloride,<sup>156, 168</sup> giving a mixture of anthroic acid and aceanthrenequinone, the latter being obtained in larger amount (60%) when aluminium chloride is present, and yielding the 1:9-carboxylic acid on oxidation.<sup>175</sup>

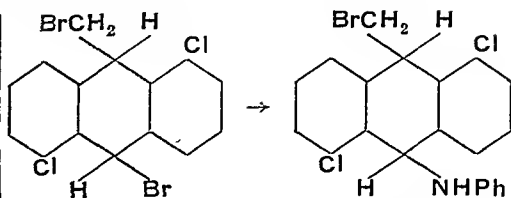
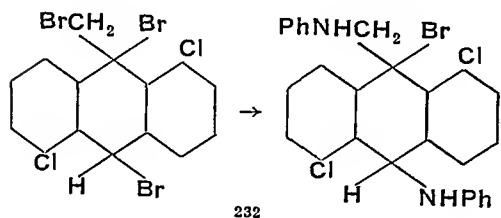
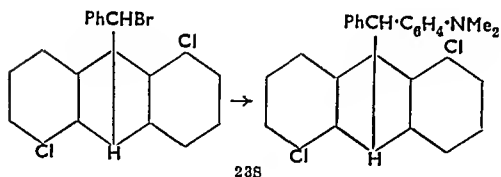
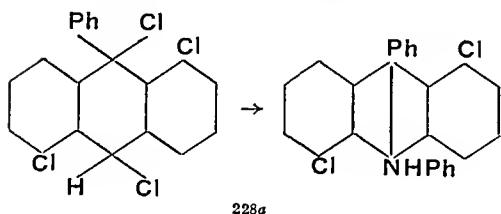
Malonyl chloride reacts similarly,<sup>173, 179</sup> whereas diethylmalonyl chloride reacts in the *Bz*-positions.<sup>147</sup> The reactions of benzoyl chloride or, better, benzoic anhydride,<sup>233a</sup> with anthracene have been studied in detail, first by Perrier, who claims to have prepared three isomers<sup>62</sup>; later workers, however, fully described anthraphenone (9-benzoylanthracene) as the main product<sup>85, 87, 209, 233</sup> with 9:10-dibenzoylanthracene as a second product. Phthalic anhydride condenses with anthracene in presence of aluminium chloride giving what is most probably *o*-anthroylbenzoic acid.<sup>137, 167, 186</sup> Maleic anhydride condenses with anthracene to give a product to which Oddy<sup>203</sup> wrongly ascribed the keto-acid structure (I):



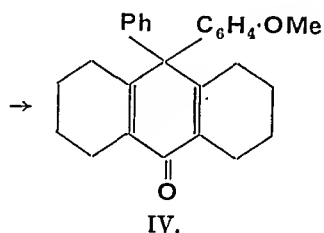
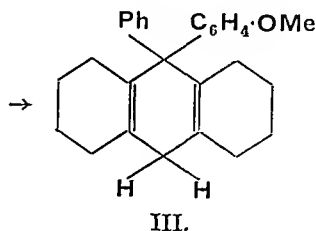
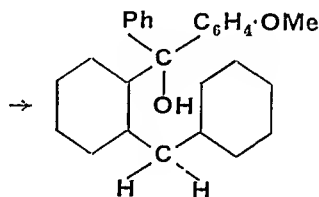
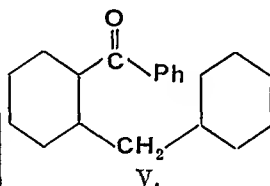
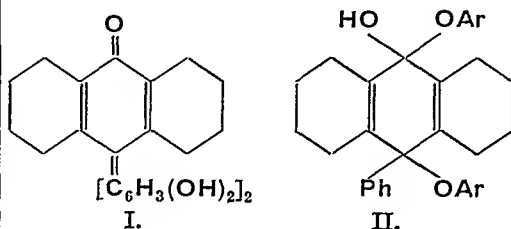


Even dichloroacetic acid (but not chloroacetic acid) undergoes this reaction to a small extent,<sup>270, 281, 283, 289</sup> and the otherwise inaccessible anthronylacetic acid can be prepared by condensing anthrone with cinnamyl chloride and oxidising with chromic acid.<sup>283</sup>

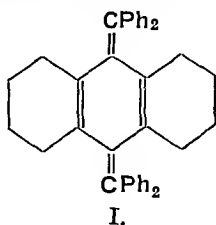
(c) *From Halogen Anthracenes and Reactive Aryl Compounds.*—9-Halogen-10-phenyl- or 9:10-dihalogen-9:10-dihydro-anthracenes (where the *Bz*-rings may also be substituted by chlorine or methyl groups) react very readily with aryl or heterocyclic compounds having a reactive nuclear hydrogen due to the presence of a powerful basic grouping, such as the *p*-hydrogen in dimethylaniline. The group may enter once with removal of halogen acid, or twice, and when the halogen is bromine it may remove halogen or halogen acid so that some monohalogen anthracene and anthracene itself are found in the products.<sup>225, 242</sup> Where *Bz*-substituents (chlorine or methyl groups) are present, and alkyl or aryl groups in the 9-position, facile condensation occurs in many cases with dimethylaniline, methylaniline, aniline, and piperidine, giving a large range of nitrogen-substituted dialkylanthracenes, and the same reactivity extends to the bromine atoms in  $\omega$ -bromomethyl-anthracenes, which can be prepared from methyl- or benzylanthracenes.<sup>228a, 232, 235, 252a, 252b, 258, 265, 266, 267, 270, 274</sup> Examples are:



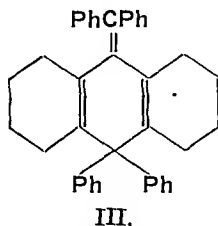
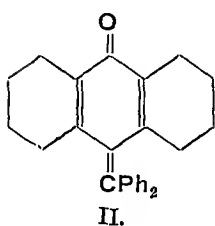
(d) *From Halogen Anthrones and Aromatic Compounds.*—The halogen atoms in monohalogenanthrones are extremely active; thus bromoanthrone with resorcinol, in absence of any condensing agent, gives tetrahydrodiphenylanthrone (I), and phenylchloroanthrone reacts similarly, although with phenol, and with cresol it is said to be substituted in the carbonyl group giving O-aryl ethers (II).<sup>113</sup> Compounds of type (I) are also obtained by heating anthraquinone with phenols, resorcinol, etc., and zinc chloride.<sup>98, 103</sup>



anthrone (II) (below).<sup>127a, 148</sup> This reaction also proceeds with *Bz*- $\beta$ -chloroanthrones, but fails with 1:8- and 4:5-dichloroanthrones, with which the corresponding dianthrones are the only pro-

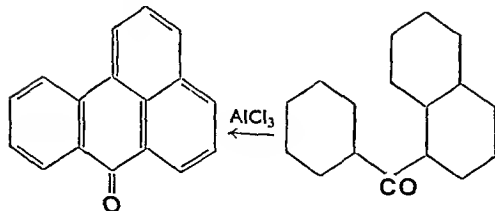
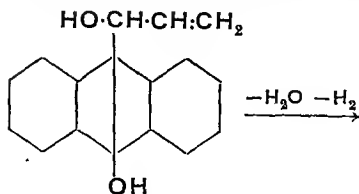


ducts.<sup>259</sup> This is another example of the effects of *Bz*- $\alpha$ -substituents on the activity of the *meso*-hydrogens.



Barnett also found that 10:10-diphenylanthrone readily condensed with benzophenone chloride giving 9:9-diphenyl-10:10-diphenylmethylene-9:10-dihydroanthracene (III).<sup>240</sup> The double bond in the latter was stable to reduction by zinc-acetic-hydrochloric acid, to sodium and amyl alcohol, and to hydriodic acid and phosphorus.

The reaction of aldehydes with anthrone is, however, a very general reaction and also occurs under other conditions, such as in 82% sulphuric acid. There is also the complication that when the carbon chain of the aldehyde is of three or more carbons, there is a tendency to form a new benzene ring between the *meso*-carbon and the *peri*-carbon. This is manifested by Bally's fundamental discovery of the benzanthrone\*



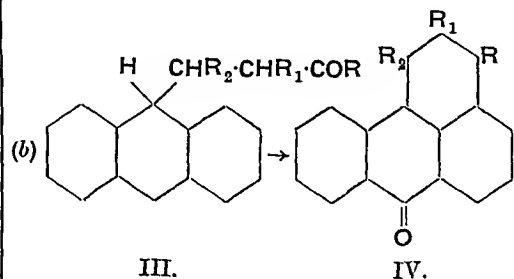
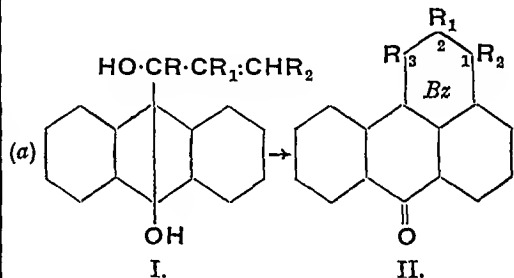
\* Benzanthrone is sometimes known as 1:9-benzanthrone. By the nomenclature of the present memoir it would be named 4:10-benzanthrone. It is also called *ms*-benzanthrone, but the latter is open to objection as description of a ring as "*ms*-benz" does not express the fact that this benzene ring is fused to the system by three common carbon atoms.

reaction. This is carried out by heating anthrone, or anthraquinone and a reducing metal, in 82% sulphuric acid, with glycerol.<sup>111</sup> The reaction was elucidated by Bally and Scholl<sup>158</sup> and explained as an aldol condensation of anthranol with acrolein followed by loss of water and dehydrogenation.

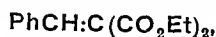
The Bally-Scholl benzanthrone synthesis was checked by a new "*peri* ring-synthesis," due to Scholl and Seer, by fusing phenyl- $\alpha$ -naphthyl ketones with aluminium or ferric chloride.<sup>166</sup>

The benzene ring formation is encouraged by the 82% sulphuric acid, but it can be separated into a condensation and a ring-closure stage under certain conditions. It is to be noted however, that  $\alpha\beta$ -unsaturated ketones of the type  $R\cdot CO\cdot CR_1\cdot CHR_2$  may condense with anthrone by one of two possible mechanisms:

- when  $R=H$ , generally by the aldol mechanism suggested by Bally and Scholl, to yield a condensation product (I) and by ring-closure a substituted benzanthrone (II);
- when  $R$  is not hydrogen, by a Michael addition to the double bond giving a condensation product (III) which on ring-closure gives the oppositely substituted benzanthrone (IV).



Very frequently the group  $R_1$  is split off in the condensation. This possibility was first foreseen by Meerwein,<sup>188</sup> who indeed condensed anthrone with diethyl benzylidenemalonate



ethyl benzylideneacetoacetic ester

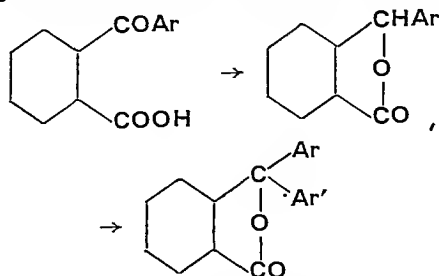


and benzylideneacetophenone



to yield the Michael addition products, which, however, were in general too unstable for ring-closure to be carried out. The first was, how-

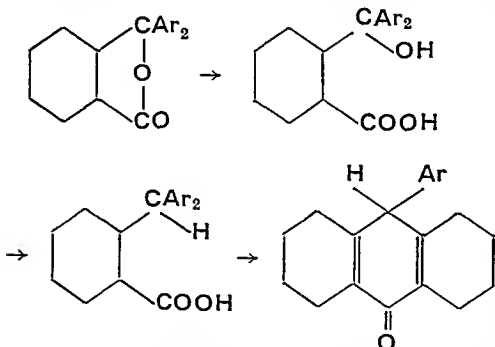
Monoarylpthalides are prepared by reduction of phthaloylic acids, <sup>45, 76, 81a, 83, 96, 240, 277</sup> and by the Friedel-Crafts reaction with aromatic hydrocarbons they yield diarylpthalides.<sup>45, 226</sup>



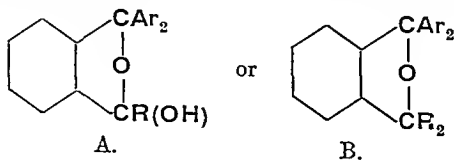
Diarylpthalides in which one aryl has a tertiary amino-group are often quantitatively obtained by adding a tertiary amine (with free *p*-position) to the phthalide (from the acid and acetic anhydride)<sup>72, 93</sup>; when a *m*-hydroxy-tertiary amine is used, no condensing agent at all is required.<sup>93</sup>

Phthalic anhydride in some cases gives good yields of diarylpthalides [e.g., diphenyl- (III), dimethyl-, diethyl- and dibenzyl-phthalides] by the Grignard method.<sup>101</sup>

The diarylpthalides, when the ring is opened with alkalis, are readily reduced to the triaryl-methane carboxylic acids, which can then be dehydrated and yield monoarylanthrone.<sup>16, 72, 78</sup>



**2. Action of Grignard Reagents on Phthalides.**—The mechanism of this reaction has not been fully worked out. Two types of products are obtained :



Type (A), R=aryl, give 9:9-diaryl-9:10-dihydroanthracenes on reduction with sodium amalgam, with loss of water. If one Ar is hydrogen, a further dehydration occurs, giving a monoarylanthrone.

Type (B), if the ring is opened by alkali, can form anthracene derivatives by dehydration with sulphuric acid, and again if one Ar is hydrogen, dehydration occurs with formation of a phenylarylanthrone.

With phthalide itself (Ar=H) three molecules

of the reagent, where R=methyl, ethyl, *iso*-propyl, benzyl,<sup>132</sup> and phenyl<sup>127</sup> yield only type (B). The diol passes into the phthalane (B, Ar=H) very easily with dilute hydrochloric acid, except when R is phenyl, when the phthalane is formed only with difficulty. In this case 9-phenylanthracene is much more readily obtained by treating a benzene solution with sulphuric acid. Monoarylpthalides, being readily available, have been more fully examined, both (A) and (B) types having been observed.<sup>127, 161, 163</sup>

Diphenylphthalide, with three molecules of phenyl magnesium bromide, gives type (B), and dehydration occurs with glacial acetic acid to give tetraphenylphthalane (B, Ar=R=Ph).<sup>163</sup> When, however, diphenylphthalide is added to a large excess of phenyl magnesium bromide type (A) is obtained, and this on reduction and dehydration yields 9:10-diphenylanthracene.<sup>127</sup>

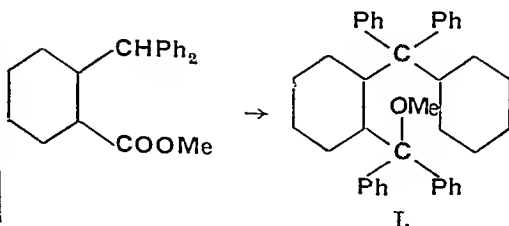
Phthalic esters act as dialkoxyphthalides and give products of type (A),<sup>127, 217</sup> the alkoxy-groups being simultaneously replaced by aryl groups. Shibata however, with methyl magnesium iodide and benzyl magnesium iodide, found that dehydration occurred with formation of methylene- and benzyldiene-dialkylphthalanes.<sup>143</sup> When phenyl magnesium bromide was used the distilled product (m.p. 194–195°) was described as diphenylphenylenephthalane on the same lines, but Barnett has shown that this substance is diphenylanthrone,<sup>240</sup> the dehydration occurring either in the distillation or by means of the excess Grignard reagent. Phthalic anhydride acts as ketophthalide and gives type (B) products with methyl or ethyl magnesium halides<sup>113</sup> and with phenyl or benzyl magnesium halides,<sup>123</sup> only two molecules of reagent being used in both these cases.

The phthaloylic esters react as arylalkoxyphthalides; for instance, methyl *o*-benzoylbenzoate gives type (A) with simultaneous replacement of the methoxy-group,<sup>123</sup> and the ethyl ester behaves similarly.<sup>240</sup>

The transformation of the products to 9:9-diphenyl-9:10-dihydroanthracene takes place as already mentioned. The yield is only 40% in the case of the ethyl ester, but *o*-benzylbenzhydrol is also formed, probably owing to the reducing action of the Grignard reagent.

### 3. Miscellaneous Methods.

**The Guyot Compounds.**—According to Haller and Guyot,<sup>104</sup> the methyl ester of triphenylmethane *o*-carboxylic acid, with phenyl magnesium bromide, gives the methoxy-compound (I), passing into 9:9:10-triphenyl-9:10-dihydroanthracene with dry hydrogen chloride.<sup>105</sup>



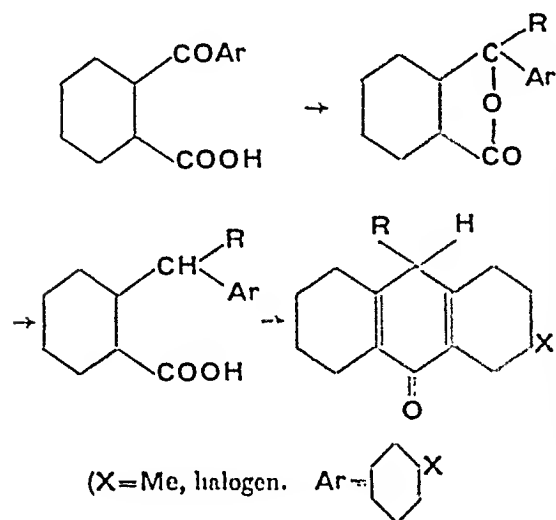
I.



Barnett, Cook, and Nixon, by obtaining the same compound whether the methyl or ethyl ester was used, have shown that (I) is really the carbinol and not the methyl ether.<sup>240</sup>

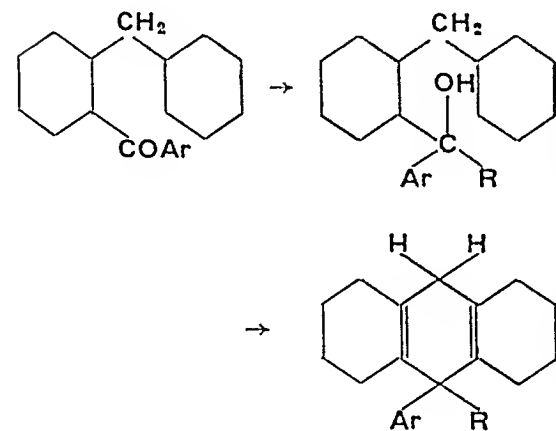
The Guyot school<sup>140, 149</sup> employing their remarkable series of dialkylaniline derivatives, prepared the 9-dialkylanilinophenyl derivatives of 2-dialkylaminoanthracene.

*Action of Grignard Reagents on Ketones.*—The *o*-aryloylbenzoic acids react normally with Grignard reagents, and the resulting isobenzofuran may be reduced to the triarylmethane carboxylic acid and cyclised to the anthrone:



Thus, the case where Ar=*p*-tolyl, R=cyclohexyl (X=Me or halogen) has recently been described,<sup>256</sup> yielding 10-cyclohexyl-2-methylanthrone, reduced by zinc and ammonia to the 9-hydroxydihydroanthracene, which was dehydrated by acetic anhydride to 10-cyclohexyl-2-methylantracene.

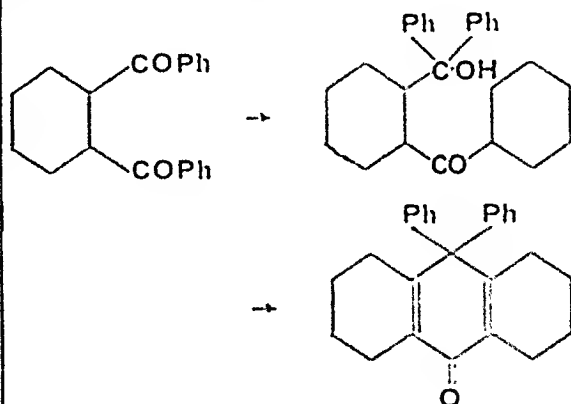
9:9-Diaryl- or alkylaryl-9:10-dihydroanthracenes are obtained by commencing with *o*-benzylphenyl aryl ketones, and treating these with a Grignard reagent to yield benzylphenyl diphenyl carbinols, which can be cyclised with acetic-hydrochloric acid.



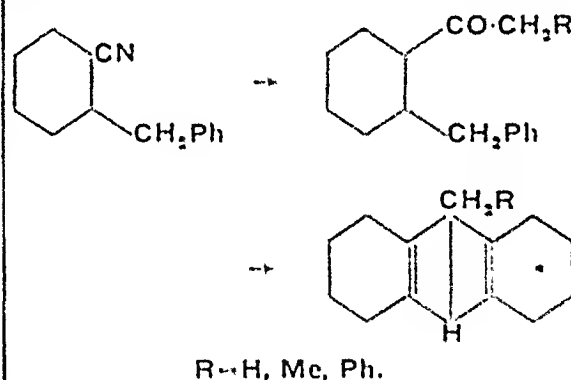
The case Ar=Ph, R=*p*-anisyl has recently been described.<sup>255</sup>

Similarly, *o*-dibenzoylbenzene, with phenyl

magnesium bromide, yields 2-benzoyltriphenyl carbinol, yielding diphenylanthrone at 300°.<sup>240</sup>



Bradsher<sup>222</sup> describes a route to alkylantracenes which has novel features. *o*-Benzylbenzonitrile, prepared by heating 2-chlorodiphenylmethane with cuprous cyanide, reacts with methyl magnesium iodide, giving *o*-benzylacetophenone. The latter, on long boiling with acetic and hydrobromic acids, gives 80% yields of 9-methylantracene; similar results are obtained when the Grignard reagent is prepared from ethyl iodide and benzyl chloride, giving 9-ethyl- and 9-benzyl-anthracene. The dehydration is probably preceded by enolisation:



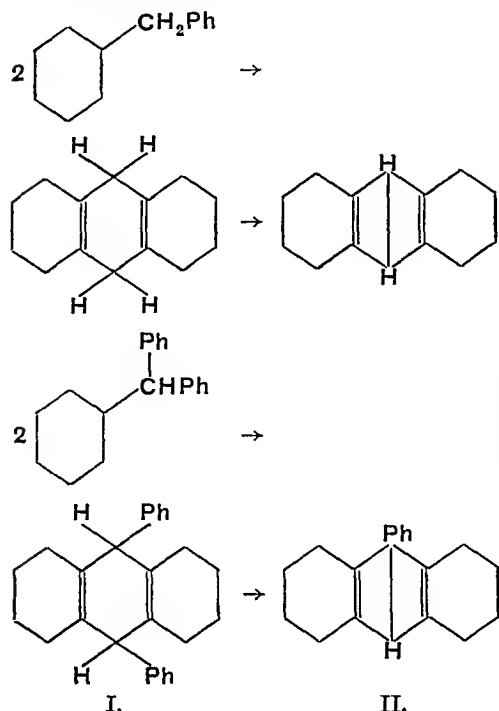
### C. SIMULTANEOUS INTRODUCTION OF ALKYL (ARYL) GROUPS AND ANTHRACENE RING CLOSURE.

It was noticed by Friedel and Crafts that 9-phenylantracene was a by-product in the preparation of triphenylmethane from chloroform, benzene, and aluminium chloride.<sup>21, 41</sup> This reaction was subsequently discussed by Linbarger<sup>69</sup>; it is similar to the formation of anthracene from diphenylmethane.<sup>197</sup>

The mechanism of the last reaction, however, is still obscure, as Barnett has shown that the conversion (I)–(II) does not occur with aluminium chloride in carbon disulphide solution, only 9:10-diphenylantracene being formed, although 9:9-diphenyl-9:10-dihydroanthracene readily splits off benzene in similar circumstances to yield 9-phenylantracene.<sup>240</sup>

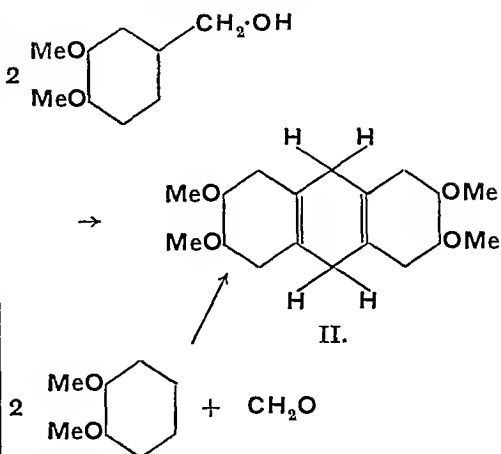
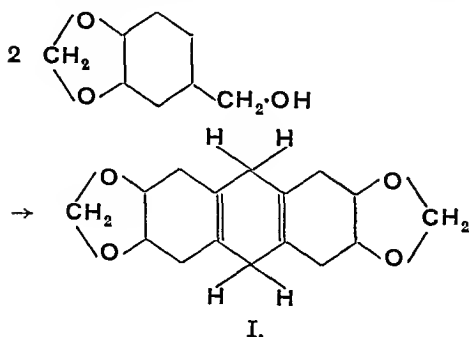
Ethylidene dibromide or dichloride, or bromoethylene, reacts with benzene or toluene and aluminium chloride to yield products originally considered to be 9:10-dimethyl-9:10-dihydro-

anthracenes,<sup>46</sup> but shown by Barnett<sup>228c</sup> to be 9:10-dimethylantracenes, because they are identical with the product obtained by methyl magnesium iodide on 10-methylanthrone; this product also forms a picrate, which dihydroanthracenes do not.

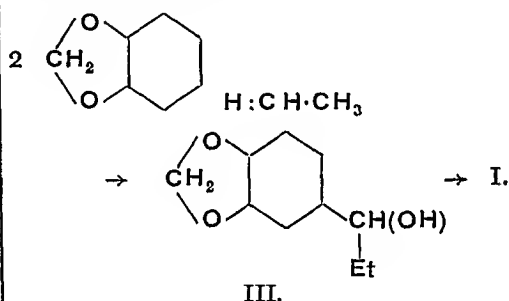


A number of reactions occur in which anthracenes, including alkylantracenes, are formed directly by the action of simple acid condensing agents on aromatic substances in which the necessary reactive groups are already present. Thus the dimer produced by Ewins<sup>145</sup> from homopiperonyl alcohol was more simply prepared by Robinson,<sup>165</sup> and its constitution shown to be dimethylene-2:3:6:7-tetraoxy-9:10-dihydroanthracene (I) as Ewins suspected.

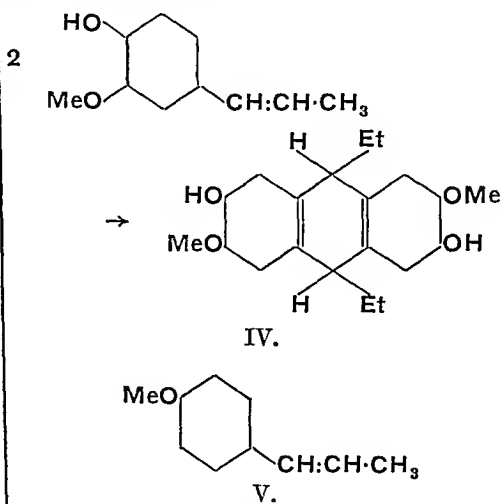
Homoveratryl alcohol gives the same reaction with equal ease, affording (II),<sup>260</sup> and when veratrol is treated with formaldehyde and 60% sulphuric acid, a theoretical yield is obtained. It is remarkable, however, that (II), on treatment with 40% nitric acid, does not oxidise to the anthraquinone, but opens the ring and nitrates to a dinitrodiphenylmethane derivative.



In the case of *isosafrole*, the anthracene formation may occur by hydration of the double bond and loss of water, (III) yielding the 9:10-diethyl derivative of (I), which should exist in *cis*- and *trans*-forms, and two apparently distinct isomers have been observed melting at  $145^\circ$ <sup>73</sup> and  $95^\circ$ ,<sup>177</sup> the latter being converted to the former by distillation.<sup>185</sup>



*iso*-Eugenol undergoes a similar transformation and the product has been shown by R. D. Haworth and Mavin,<sup>273</sup> to be (IV).



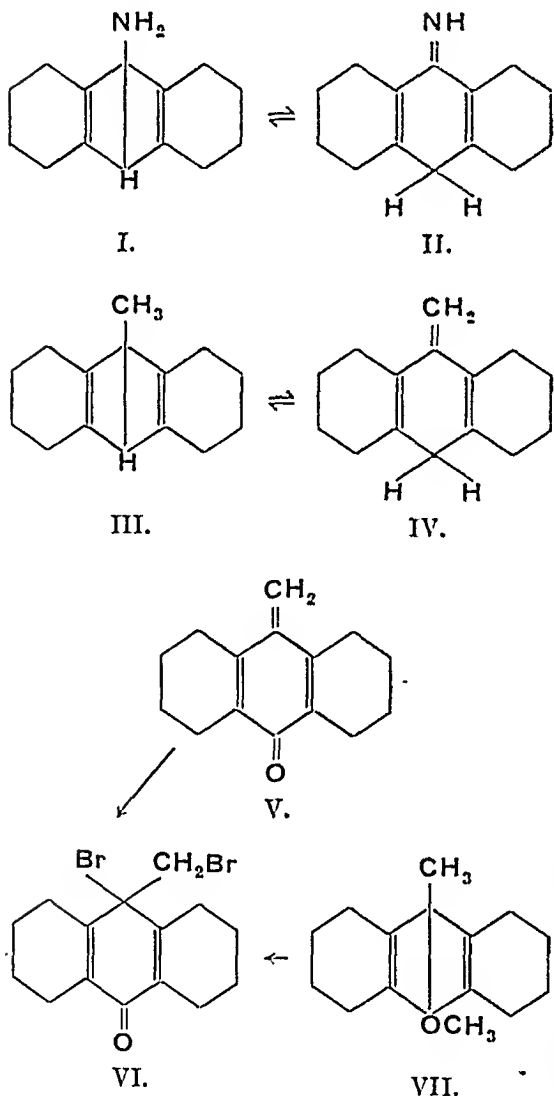
(Not reactive.)

On the other hand, anethole (V) gives no anthracene derivative by similar treatment.

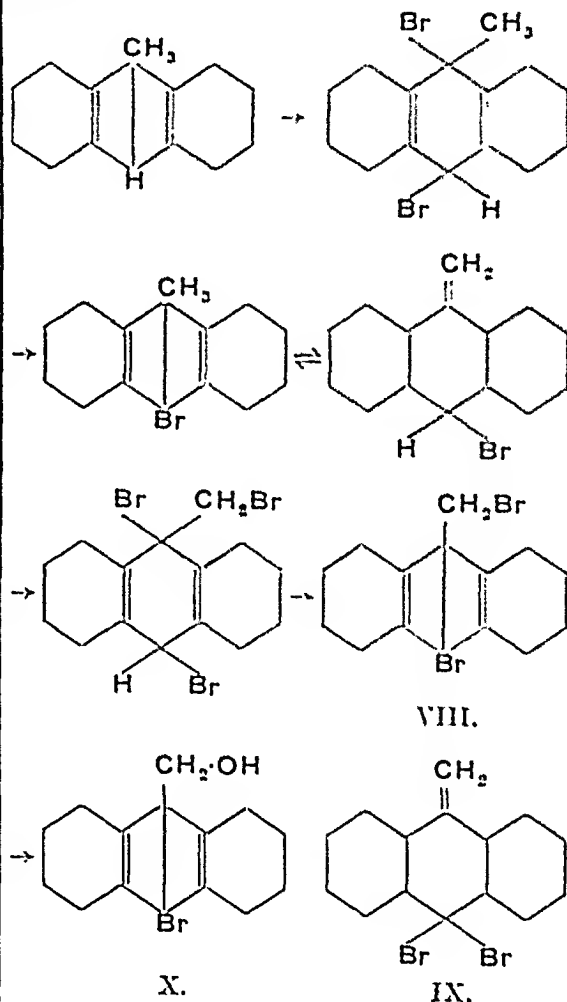
## TRANSANNULAR TAUTOMERISM\* OF 9-ALKYL ANTHRAENES.

The clarification of the anthranol-anthrone tautomerism by the researches of K. H. Meyer and his pupils, referred to above, and the supporting evidence of a similar tautomerism between 9-aminanthracene and 9-imino-9:10-dihydroanthracene<sup>131, 172</sup> (I-II), led Barnett and his school to investigate and amply demonstrate the corresponding tautomerism between 9-methylanthracene and 9-methylene-9:10-dihydroanthracene (III-IV). The common factor in these related changes of constitution is the movement of a hydrogen atom across the 9:10-positions of the central ring, hence named by Barnett "transannular tautomerism."

First evidence of a similar tendency in 9-methylanthracene derivatives was shown by the preparation of a dibromo-compound (VI) from 10-methyleneanthrone (V), which was equally well obtained by Meyer from 10-methylanthranol-9-methylether (VII),<sup>193</sup> so that its constitution must be that shown.



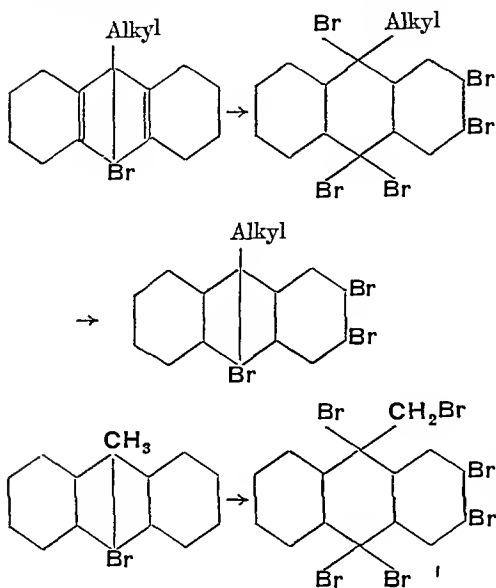
Barnett first studied the behaviour of bromination of 9-alkylanthracenes. 9-Methylanthracene gives with one molecule of bromine the 10-bromo-9-methylanthracene, probably by the addition of bromine and splitting off of hydrogen bromide, as shown, and a second molecule of bromine yields a dibromo-compound which must be the 10-bromo-9-bromomethylanthracene, as one of the bromines is very reactive and yields acetoxy- and hydroxy-derivatives. Hence it is considered to be (VIII), and not (IX), because the bromine atoms in the latter would be identical in reactions, and it would yield methyleneanthrone on hydrolysis, instead of which it gives the hydroxy-compound (X). The mechanism of bromination is most probably explained by the 10-bromo-9-methylanthracene first formed tautomerising to 10-bromo-9-methylene-9:10-dihydroanthracene, the latter then adding bromine to the double bond and undergoing transannular loss of hydrogen bromide. In addition it forms a monopyridinium salt, which could not be explained on (IX), but is clear in (VIII), owing to the active  $\omega$ -bromine atom.<sup>224</sup>



9-Ethyl-, isopropyl- and isoamyl-anthracenes do not yield dibromides of this type, but excess bromine in all cases (except 9-methylanthracene, which gives a hexabromo-compound) yields pentabromo-derivatives, which on treatment with caustic potash yield tribromo-9-alkyl-

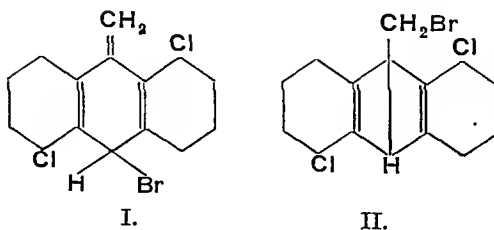
\* Bergmann<sup>257</sup> recommended that the word "transannellar" should be substituted, but Barnett's original nomenclature has been retained in this memoir.

anthracenes; two of the bromines are in the 2:3-positions and the third in the 10-position :



However, 9:10-dimethylantracene yields 9:10-di(bromomethyl)anthracene, giving a dipyridinium salt, and 10-phenyl-9-methylantracene yields 9-bromomethyl-10-phenylantracene.<sup>228c</sup>

**Influence of Bz-chloro-substituents.**—The researches now extended to the Bz-chlorinated 9-alkylantracenes, where the effects of the  $\alpha$ -chlorines were already known to be powerful. 9-Methyl-1:5-dichloroanthracene gives a monobromo-compound in which the bromine is attached to the methyl group and not to the 10-carbon. This would be expected, because the 10-hydrogen is already to some extent protected by co-ordination with the 5-chlorine atom, according to previous knowledge. The bromine of the bromomethyl group is very active. It yields 9-alkoxymethyl-derivatives by heating with the corresponding alcohols, and the acetoxymethyl compound with sodium acetate. It also yields a dimethylaminophenyl derivative with dimethylaniline, and a pyridinium salt with pyridine. It can have either the methylene-dihydroanthracene (I) or the bromomethylantracene structure (II), but the former would probably be colourless, and as the substance is a bright yellow, this points to (II) for the solid form.

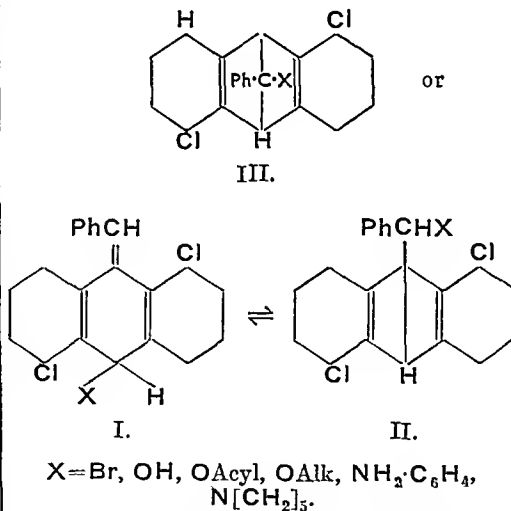


However, in its reactions it is shown to behave as two different substances. The acetoxy-compound above, m.p. 149°, can be hydrolysed to a hydroxy-compound, m.p. 139°, which

regenerates the same acetoxy-compound with acetic anhydride in pyridine. But if the bromo-compound is delicately hydrolysed with aqueous acetone and calcium carbonate, a hydroxy-compound is obtained, melting at 133–134°, unchanged by recrystallisation, and depressing the melting point of its isomer, showing that it is different in structure. On the other hand, by acetylation the same acetyl compound, m.p. 149°, is regenerated. The two hydroxyl derivatives also regenerate the bromo-compound with hydrobromic acid, but they give with phenyl isocyanate two different phenylurethanes, one melting at 179° (from the hydrolysed acetate), and the other at 193° (from the hydrolysed bromo-compound). The latter is colourless, the former yellow.<sup>232</sup> Consequently the tautomerism of the bromo-compound ( $I \rightleftharpoons II$ ) is established, and it seems most likely that the colourless compounds possess structure (I) and the yellow compounds structure (II).

1:5-Dichloro-9-ethylantracene gives a similar series of derivatives, the presence of the chlorine atoms enabling the  $\alpha$ -carbon to be brominated.

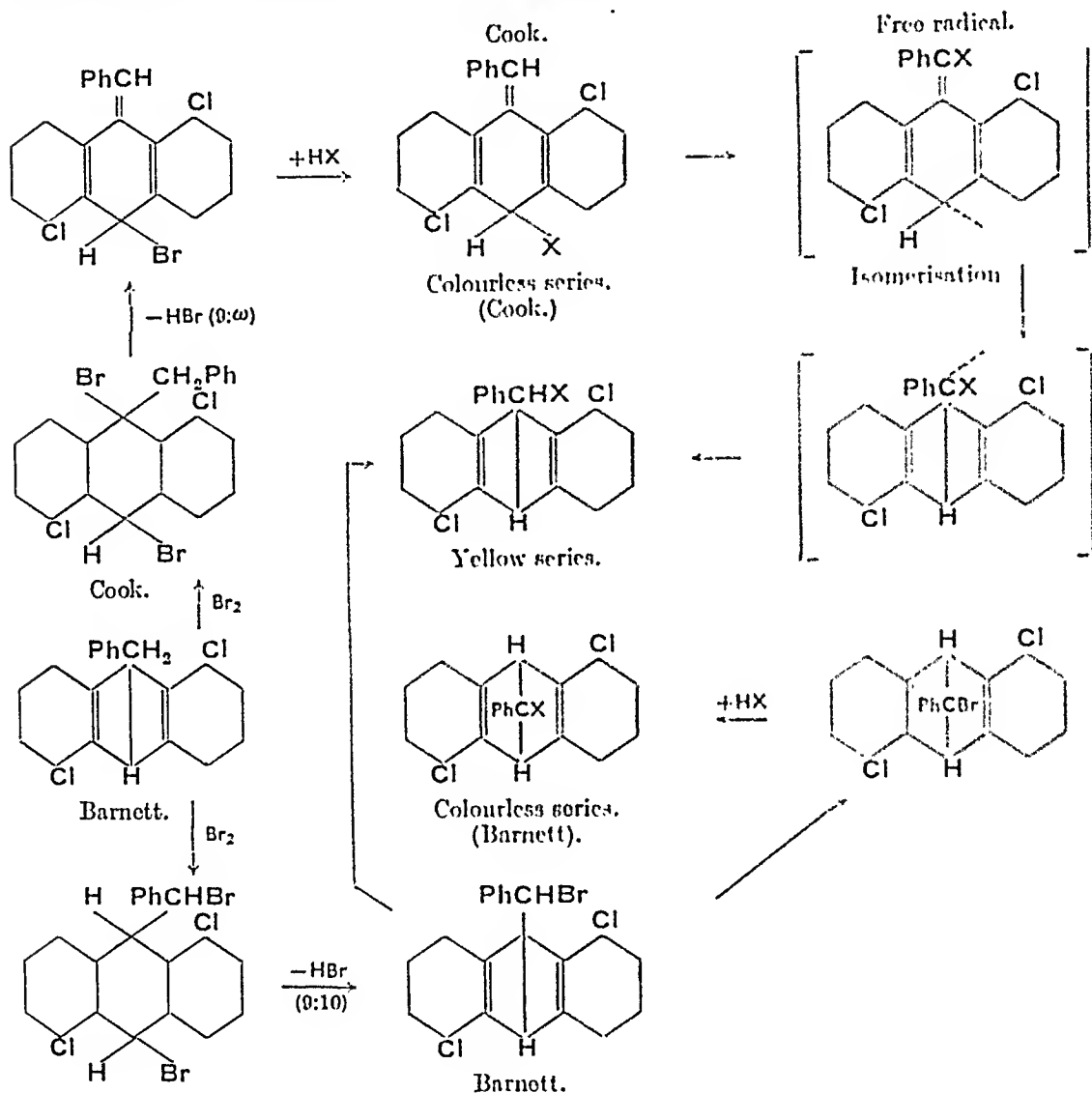
Cook had already shown that 9-benzylantracene resembled 9-ethylantracene in giving the 10-bromo-compound by bromination,<sup>233c</sup> but again, with 1:5-dichloro-9-benzylantracene the behaviour is different. Here again two series, of yellow and colourless compounds, are obtained, which clearly could be defined as before by the tautomerism ( $I \rightleftharpoons II$ ).



When the transformations of the monobromo-compounds to the derivatives are kept neutral by calcium carbonate, except where sodium acetate is used for a short heating in acetic acid, the resulting derivatives are colourless, but all of them are easily changed over to the yellow varieties by careful treatment with acids; both the yellow and the colourless hydroxy-compounds give the same original bromo-compound with hydrobromic acid. In the case of the 9-methylantracenes and the corresponding 1:5-dichloro-derivatives, an isomerisation undoubtedly takes place first, although the hydroxy-compounds give the same acetoxy-derivative. Thus formulæ (I–II) would demand

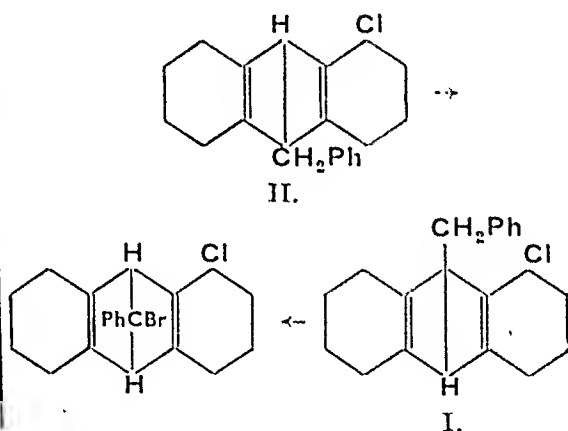
the transannular migration of the group X. Barnett was at first inclined to regard this as unlikely, and thus was led to propose an endocyclic structure<sup>238</sup> for the colourless compounds (III), recalling earlier suggestions for anthracene derivatives<sup>116, 116a, 191, 198, 211</sup> and the undoubted endocyclic types later discovered by addition of maleic and other acids to anthracene, where, however, the endocyclic ring contains

one more carbon. The alternative view of Cook<sup>239, 249</sup> was that (I  $\rightleftharpoons$  II) was the correct interpretation, and that the facile change of a derivative of type (I) to one of type (II) could occur by fission of the group X, and its addition in the new position. Cook considered that the bromine in Barnett's proposed endocyclic type (III) would be less active than is the case, the constitution thus being rendered unlikely.

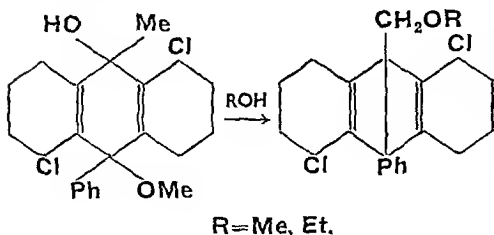


The proof of the correctness of the second view, and that alkoxy-groups could indeed migrate across the ring, came later.<sup>248, 251</sup> Thus if the endocyclic structure is correct, 1-chloro-9-(I) and 1-chloro-10-benzylanthracene (II) should yield the same bromo-compound.

Cook showed<sup>248</sup> that (I) and (II) behaved quite differently on bromination, the former giving mostly the 10-bromobenzylidene type, which could be converted to both colorless and yellow types of derivatives; the latter yields a bromo-compound which gives only yellow-type derivatives. In this case the movement of groups into the 9-position is probably hindered by the 1-chlorine atom, and the  $\omega$ -bromo-compound is the stable form in this case, just as

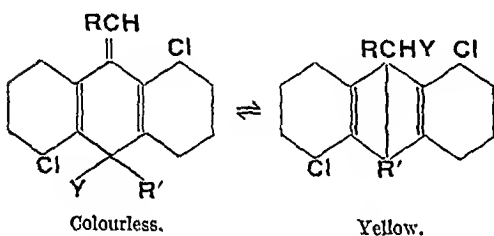


in the former the 1-chlorine atom renders the 10-bromobenzylidene type the stable tautomer. The proof of the migration of O-alkyl groups was supplied by Barnett<sup>251</sup> and Cook (*l.c.*). Thus, colourless 1:5-dichloro-9-hydroxy-10-methoxy-10-phenyl-9-methyl-9:10-dihydroanthracene (in which no free hydrogen atoms are present to complicate the isomerisation), on treatment with methyl-alcoholic hydrochloric acid, is converted into a greenish-yellow fluorescent substance, 1:5-dichloro-9-(methoxymethyl)-10-phenylanthracene, m.p. 154°.



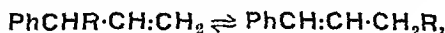
This proves that the O-alkyl group can wander from the 10- to the  $\omega$ -methyl position. If ethyl-alcoholic hydrochloric acid is used, the migrating group becomes ethoxymethyl.

The accepted isomerisation is therefore expressed in the scheme:



Cook has advocated the theory that ionic dissociation in solution occurs prior to any transformation, and points out analogies to the simplest three-carbon systems investigated by other workers, such, for instance, as the re-

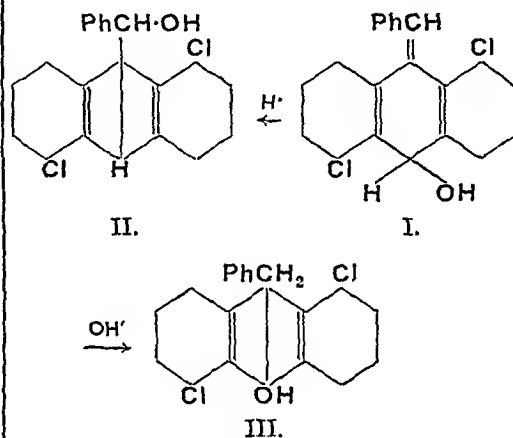
actions of the  $\alpha$ -phenylalkyl systems investigated by Burton,<sup>246</sup>



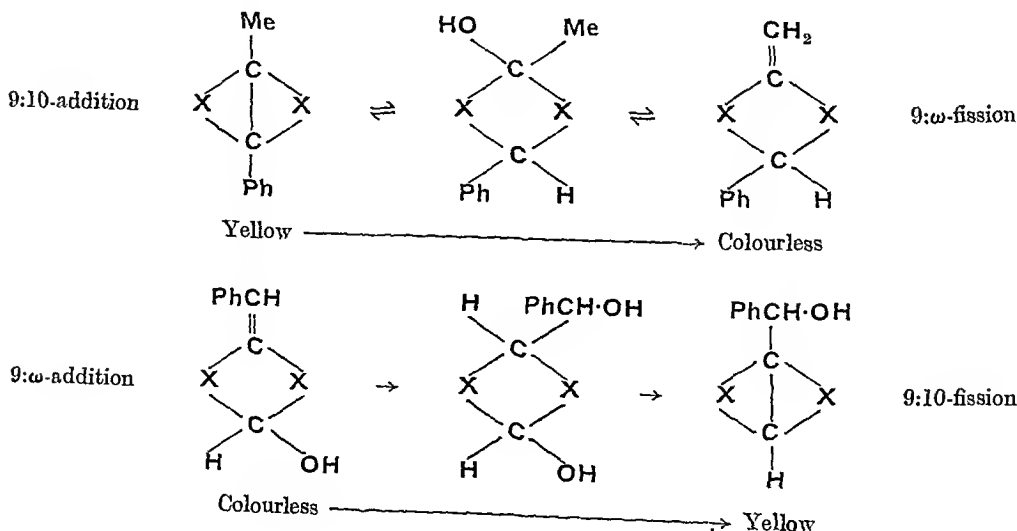
where the mobility of the anion R



follows exactly the same order as in the compounds here discussed. Further, the ionic hypothesis is supported by the fact that the presence of hydrogen ions favours migration of hydroxy groups (as in the experiment just discussed), i.e. (I  $\rightarrow$  II) (e.g., conversion of colourless hydroxy-compounds to the yellow form by mineral acid), while hydroxyl ions favour the movement of hydrogen (as, for instance, in all anthrone  $\rightarrow$  anthranol conversions) exemplified by Cook's experiment in which 1:5-dichloro-10-hydroxy-9-benzylidene-9:10-dihydroanthracene (I) is converted by boiling caustic soda solution into 1:5-dichloro-10-benzylanthranol (III).



Barnett points out<sup>252a</sup> that the same effects could be produced by hypothetical addition of the elements of water across the 9:10-positions, followed by splitting off water from the  $\omega$ - and adjacent positions, or vice versa:

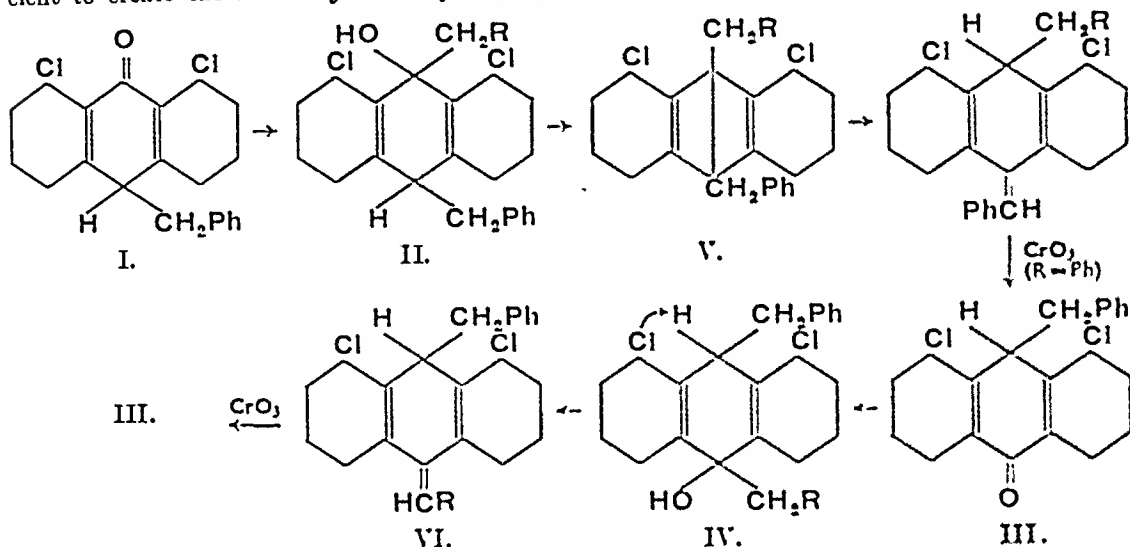


Extending the investigation to 1:4-dichloro-9-benzylanthracene,<sup>252a</sup> Barnett found similar results, bromination giving a stable 10-bromo-derivative of the benzylidene structure, which yields colourless derivatives under neutral conditions, and a yellow acetoxy-derivative in acetic acid; the colourless derivatives are changed to the yellow by mineral acid under mild conditions.

Meanwhile it was shown that the chlorino atom in *p*-chlorobenzylanthracene is not sufficient to create the necessary mobility, as the

monobromo-derivative is unreactive,<sup>252c</sup> and in 1:5-dichloro-9-*p*-chlorobenzylanthracene the behaviour was identical with that of 1:5-dichloro-9-benzylanthracene, so that the *p*-chlorine atom has no influence at all.

The case of the 1:8- and 4:5-dichloroanthrones and their alkyl derivatives is interesting, as it is complicated by the effects of the  $\alpha$ -chlorines on hydrogens in the adjacent *meso*-positions. This effect in one of the cases to be considered is enough to prevent transannular loss of water in the carbinols arising from Grignard reactions



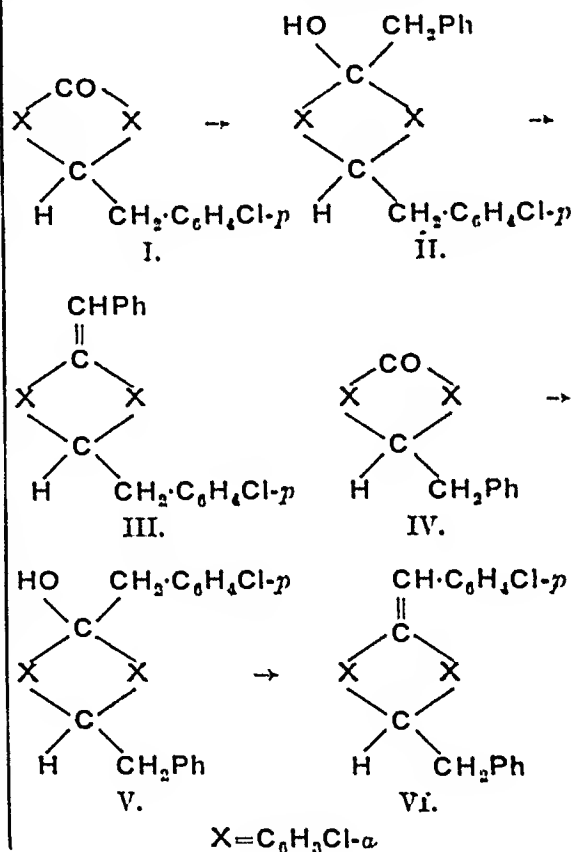
on the alkylanthrones, and instead, water-splitting occurs from the 9-hydrogen atom and the  $\alpha$ -hydrogen of the alkyl group on the same position.

The two anthrones mentioned were first alkylated by means of caustic potash and benzyl chloride to the 10-benzylanthrones (I, III), and the latter treated either with magnesium methyl iodide or with magnesium benzyl chloride. This resulted in the two dihydroanthracenes (II) and (IV) ( $R=H, Ph$ ).

In the case of (IV), the 4- or 5-chlorine atom immobilises the 10-hydrogen, and water is thus split from the only other available position, viz. the 9- $\alpha$ -hydrogen, giving the alkylidene derivative (VI), which is identified by its oxidation to the original anthrone (III). In the other case, transannular loss of water occurs because a yellow fluorescent solution is obtained when the usual dehydrating agent, acetic-hydrochloric acid, is used, but this very quickly tautomerises to an alkylidene derivative also, identified by its oxidation to the same anthrone, (III). The fact that the alkylidene form is the stable one in this case is probably also a co-ordination effect, as the 1- or 8-chlorine atom, by immobilising the hydrogen on the 9-position, can greatly hasten the conversion of the dialkylanthracene tautomer to the alkylidene-alkyldihydroanthracene.<sup>252b</sup>

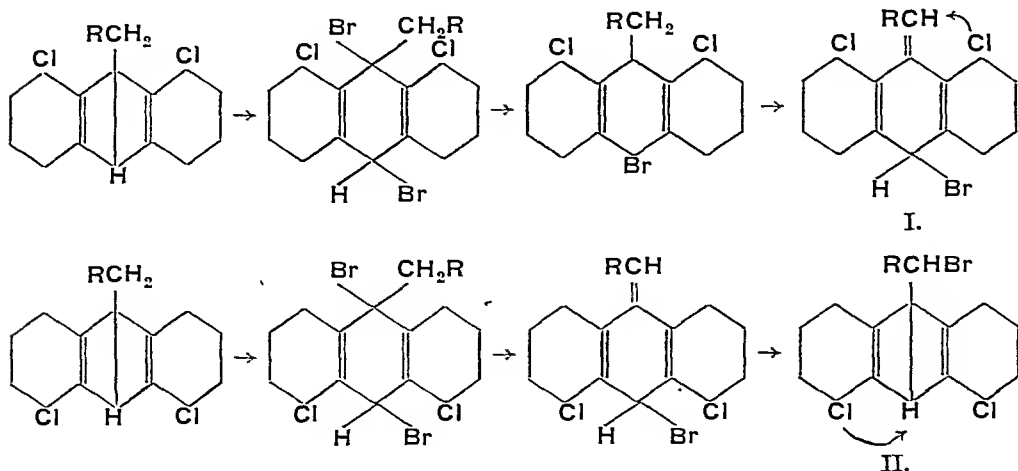
Barnett found that the two very closely related substances (III) and (VI), obtained by the synthesis shown below from 1:5-dichloroanthrone, showed little or no tendency for tautomeric change on long heating with acetic-hydrochloric acid.

This is again probably due to the 5-chlorine atom so immobilising the 10-hydrogen that the alkylidene forms shown are stable.<sup>252c</sup>



The co-ordination effects so clearly demonstrated in the derivatives of 4:5- and 1:8-dichloroanthrones were carefully developed in as complete a manner as possible by Barnett and his school. One method was by examining the behaviour of the unstable bromine addition

products of 1:8-dichloro- and 4:5-dichloro-9-alkylanthracenes. Thus the 1:8-series give as the stable product the 10-bromo-9-alkylidene-9:10-dihydroanthracenes (I), while the 4:5-series give the 9- $\omega$ -bromoalkylanthracenes (II):



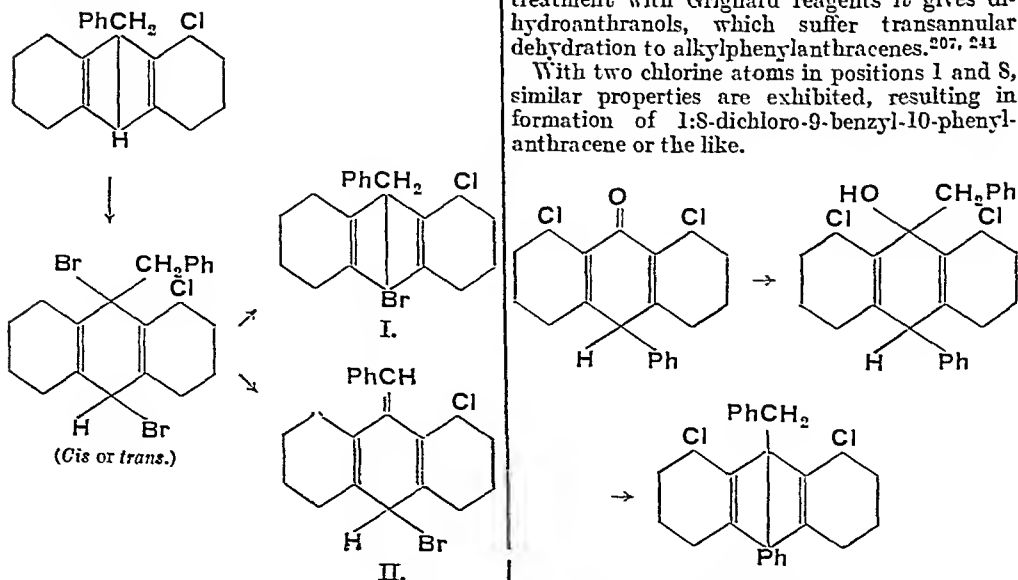
The bromine atom is in each case repelled as far as possible from the  $\alpha$ -chlorines, and the latter binds either the  $\alpha$ -hydrogen in the alkyl group in (I), or the 10-hydrogen in (II). The wandering of a bromine atom in the latter case is a remarkable phenomenon; it was already noted in the similar case of 1-chloro-9-benzylanthracene, investigated by Cook, in which case, however, both forms are isolated and there is no tendency for interconversion, probably because of the geometrical configuration of the dibromide.<sup>248</sup>

groups are not mobile, as they are stable to long heating with acetic-hydrochloric acid.

Further illustrations of the influence of the  $\alpha$ -chlorines follow.

Whereas 10-hydroxyanthrone enolises immediately to anthrahydroquinone, even on heating with water,<sup>231</sup> this is scarcely affected by chlorine at 1- or 8-positions, or both, but profoundly hindered by chlorine at 4- or 5-positions, or both. 10-Phenylanthrone, when no co-ordinating chlorine is present, behaves normally, enolising and giving an acetate; on treatment with Grignard reagents it gives dihydroanthranols, which suffer transannular dehydration to alkylphenylanthracenes.<sup>207, 241</sup>

With two chlorine atoms in positions 1 and 8, similar properties are exhibited, resulting in formation of 1:8-dichloro-9-benzyl-10-phenylanthracene or the like.

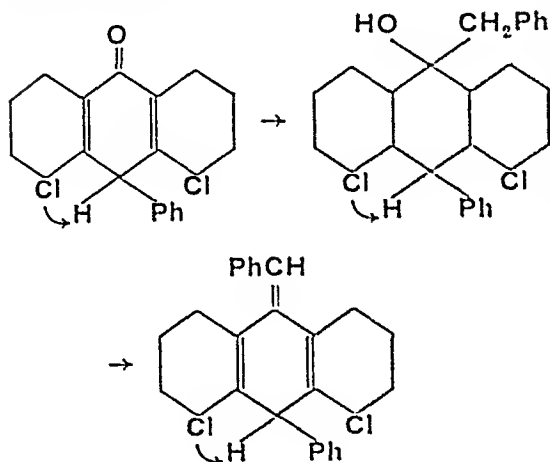


The bromines in both (I) and (II) are reactive and can be replaced in the usual ways, the derivatives of (I) being colourless and those of (II) yellow and fluorescent, but the substituent

The isomeric 4:5-dichloro-10-phenylanthrone, however, behaves very differently. It gives no acetate, and the dihydroanthranol obtained from it with magnesium benzyl chloride dehydrates in the 9- $\omega$ -positions to give 4:5-



dichloro-9-benzylidene-10-phenyl-9:10-dihydroanthracene.



With single chlorine atoms present, the 1-chloro-10-phenylanthracene is not affected, and eventually gives by the above normal procedure 1-chloro-9-benzyl-10-phenylanthracene. The isomeric 4-chloro-10-phenylanthracene is a co-ordinated compound, and therefore can yield the 4-chloro-9-benzylidene-10-phenylanthracene by 9- $\omega$ -dehydration of the dihydroanthracene, but owing to the unsaturated nature of the 10-phenyl grouping adjacent to the co-ordinate link, it is also sufficiently neutralised to make possible the anthracene bridge-bond formation by transannular dehydration, so that both forms are here obtained,<sup>258a</sup> and the case is similar to that of 1:5-dichloro-10-phenylanthracene.<sup>241</sup>

1:8-Dichloroanthracene, by condensation with benzyl chloride,<sup>252b</sup> yields only a monobenzyl derivative. Although in the present discussion no grounds exist for the hope, it was thought that 10-*o*-chlorobenzylanthracene might be all that would be produced from anthracene and *o*-chlorobenzyl chloride, thus showing a co-ordination link due to chlorine *ortho* to the benzyl group. Strangely enough, the reagent yields 1:8-dichloro-10:10-di-*o*-chlorobenzylanthracene, and the matter was not further pursued.<sup>258a</sup>

1:5-Dichloroanthracene gives only a mono-*o*-chlorobenzyl derivative, 1:5-dichloro-10-*o*-chlorobenzylanthracene, but it is impossible from the properties of this substance to reach a definite conclusion that the 5-chlorine prevents the reaction of the second molecule of benzyl chloride. The compound does not acetylate by the usual pyridine-acetic anhydride method, even on refluxing, but the reaction proceeds by addition of alcohol. From the red colour produced by alkali, it is suspected that the 10-hydrogen is reactive in an unexpected way, both in 1:5-dichloro-10-benzylanthracene and in 1:5-dichloro-10-*p*-chlorobenzylanthracene.<sup>252c, 258a</sup>

4:5-Dichloroanthracene gives also a mono-*o*-chlorobenzylanthracene which, as expected, gave no coloration with alcoholic alkali and could not be acetylated. 1:8-Dichloro- and 4:5-dichloro-10-alkoxyanthracenes are readily prepared by heating the corresponding bromoanthracenes with an alcohol in presence of calcium carbonate. Both onolise in cold alcoholic alkali,

and both acetylate easily, the reaction being more rapid with the 1:8-dichloro-compound. This is clearly due to the unsaturated character of the alkoxy-group lowering the potency of the co-ordinate link between the *meso*-hydrogen and the 4- or 5- chlorine atom.<sup>256c</sup>

Bz-Chloro-10-nitroanthracenes are readily prepared by treating the corresponding anthracenyl acetates with nitric acid in acetic acid solution.<sup>205a</sup> By treating the Bz-chloro-10-nitroanthracenes with pyridine-acetic anhydride at ordinary temperature, the 10-nitroanthracenyl acetates are obtained rapidly, provided no chlorine is present in the 4- or 5- positions. Thus acetates are readily prepared from 10-nitroanthracene itself<sup>205a</sup> and from 1-, 2- and 3-chloro-10-nitroanthracenes, but not from 4-chloro-, or 1:5- or 4:5-dichloro-10-nitroanthracenes. The last compound, which is unchanged in 17 hours at ordinary temperature, gives an unexpected result; all the other nitroanthracenes examined until now suffer extensive decomposition with pyridine, and acetylation in presence of this reagent is feasible only because the reaction is rapid and usually complete in three minutes. No acetate was obtained from 1:8-dichloro-10-nitroanthracene in spite of the absence of chlorine in 4- or 5- positions, which means that no co-ordinate link can be formed. Possibly steric hindrance is responsible, the 1:8-chlorines protecting the 9-hydroxyl so that the decomposition by pyridine is the main reaction.

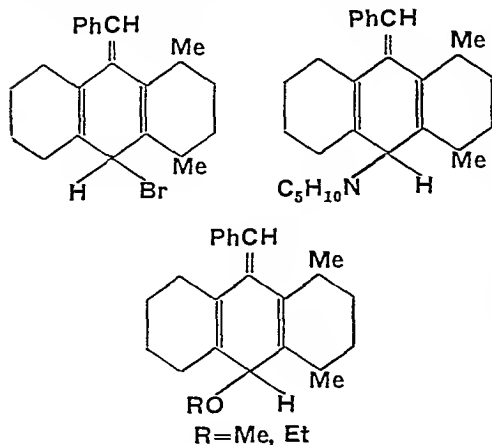
**Influence of Bz-Methyl Substituents.**—It was not expected that *o*-methyl groups would have a similar influence to *o*-chlorine atoms in promoting co-ordination effects. However, 10-bromo-1:4-dimethylanthracene easily yields a 10-methoxy-compound,<sup>125</sup> and reacts with bases (piperidine, aniline, methylaniline, and dimethylaniline) with formation of nitrogenous derivatives.<sup>192, 225</sup>

The 10-bromo-compound easily undergoes a Friedel-Crafts reaction with benzene, and the resulting 1:4-dimethyl-10-phenylanthracene gives, by a Grignard reaction with magnesium methyl iodide or magnesium benzyl chloride, dihydroanthracenes (not isolated), which by catalytic reaction of hydrogen ions do not suffer transannular dehydration, but alkylidene formation occurs, giving colourless, non-fluorescent compounds, identified by oxidation back to 1:4-dimethyl-10-phenylanthracene.

The formation of an alkylidene compound is not possible when the methyl or benzyl group is replaced by phenyl; water is then split off by the normal transannular method, and the 9:10-diphenyl-1:4-dimethylanthracene results. Further, 9-benzylidene-10-phenyl-1:4-dimethyl-9:10-dihydroanthracene, on heating with acetic-hydrochloric acid, gives a yellow, strongly fluorescent substance, but this was not obtained in good crystalline form.

The 1:4-dimethyl-9-alkylanthracenes (alkyl = methyl, phenyl) are obtained in the usual way from 1:4-dimethylanthracene. The 1:4-dimethyl-9-benzylanthracene gives a monobromo-compound which affords colourless, non-fluorescent compounds with piperidine and with methyl and ethyl alcohols. The latter tautomerise in acid solution to yellow fluorescent substances which

do not crystallise in a pure form, but on analogy with the 1:5- and 1:4-dichloro-compounds<sup>238, 239, 251, 252a</sup> have the structure 9- $\omega$ -alkoxybenzyl-1:4-dimethylantracene.



Von Braun and Bayer<sup>229</sup> reported failure to acetylate 1:4-dimethylantracene, but the pyridine-acetic anhydride method readily succeeds, although the corresponding 1:4-dimethyl-10-phenylanthranyl acetate could not be formed even on long heating, so that here the methyl groups give rise to even greater resistance than chlorines in the same positions.<sup>223a</sup>

1:4-Dimethylantracene, obtained by reducing 1:4-dimethylantracene to the dihydroanthranol with zinc and ammonia, and then dehydrating by the usual method, adds on bromine giving an unstable dibromide. This dibromide at ordinary temperature splits off hydrogen bromide slowly, and by heating in benzene, loses both bromine and hydrogen bromide, thus resembling the unstable anthrone dibromide<sup>212</sup> more than the unstable dibromides of 1:4- and 1:5-dichloroanthracenes.<sup>265</sup>

It is clear from the above that in spite of the impossibility of a co-ordinate *peri*-link being formed in derivatives of 1:4-dimethylantracene, the latter resemble the 1:4-, 1:5-, and 4:5-dichloroanthracenes, whereas 1:5-diphenoxyanthracene<sup>258b</sup> derivatives are more similar to anthracenes themselves.

Methyl groups in the  $\beta$ -positions exert effects also. 2:3-Dimethylantracene reacts normally with Grignard reagents (methyl, benzyl), and the dihydroanthranols, without isolation, give by the usual methods 2:3:9-trimethyl- and 2:3-dimethyl-9-benzylantracene.<sup>266a</sup> The latter readily gives a monobromo-compound, 10-bromo-2:3-dimethyl-9-benzylantracene, in which the bromine is not reactive. In this, 2:3-dimethyl-9-benzylantracene differs from 1:4-dimethyl-9-benzylantracene, for the latter gives the benzylidene-dihydroanthracene form.

10-Bromo-2:3-dimethylantracene shows distinct, though slight, resemblance to the  $\alpha$ -derivatives (Barnetts " $\alpha$ -properties"). It reacts with piperidine, aniline, and dimethylaniline giving nitrogen derivatives (*cf.* <sup>199</sup>), and although it resembles 10-bromoanthrone in that on long heating with methyl alcohol it gives impure and feebly soluble substances, it gives the pure

methoxy-derivative on 15 minutes heating, a length of time which even with an anthrone having real " $\alpha$ -properties" would be wholly insufficient, and with 10-bromoanthrone almost excessively long.

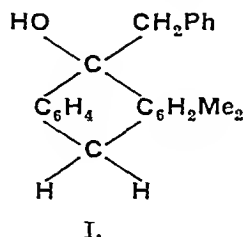
Further, 10-bromo-2:3-dimethylantracene reacts with benzene by the Friedel-Crafts reaction, giving 2:3-dimethyl-10-phenylantracene, which is easily acetylated and methylated and thus resembles phenylantracene<sup>207</sup> more than 1:5-dichloro-10-phenylantracene,<sup>228a</sup> 4:5-dichloro-10-phenylantracene,<sup>258a</sup> or 1:4-dimethyl-10-phenylantracene.<sup>265</sup>

Grignard reagents (methyl, benzyl) react with 10-phenyl-2:3-dimethylantracene and the products yield anthracenes by dehydration, whereas the 1:4-dimethyl-10-phenylantracene, discussed above, gives only the alkylidene-dihydroanthracene. 2:3-Dimethylantracene also is sharply distinguished from 1:4-dimethylantracene in its behaviour on bromination. It readily reacts with two molecules of bromine, and on standing at ordinary temperature yields rapidly the 9:10-dibromo-derivative, whereas 1:4-dimethylantracene does not give a trace of bromination product with two molecules of bromine in carbon disulphide in 24 hours at ordinary temperature.

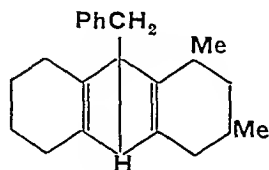
10-Bromo-2- and 3-methylantracenes were similarly investigated.<sup>266b</sup> Here, although both react with dimethylaniline to give dimethylaminophenyl derivatives, only the first gives a piperidine derivative, as 10-bromo-3-methylantracene with the latter yields 10-bromo-3:3'-dimethyldiantracene, thus resembling 10-bromoanthrone very closely; the product splits off bromine and not hydrogen bromide, yielding dianthrone.<sup>199</sup>

1:3- and 2:4-Dimethylantracenes were similarly studied. As it has been found that the 2-methyl and 3-methyl groups had only a slight influence on the properties of 10-bromoanthrone, this was expected to show which of the methyl groups in 1:4-dimethylantracene had the most influence on its properties.<sup>267</sup>

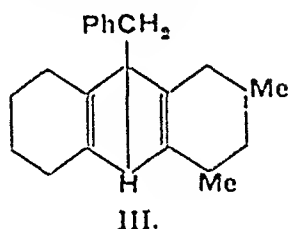
Both 1:3- and 2:4-dimethylantracenes reacted with benzyl magnesium chloride to give dihydroanthranols (I), dehydrated easily to the dimethylbenzylantracenes (II, III).



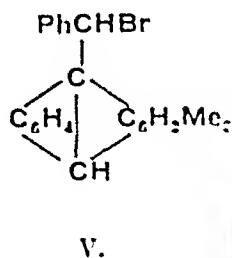
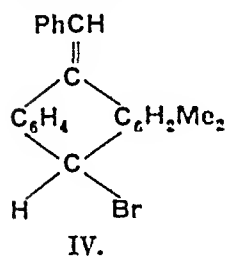
I.



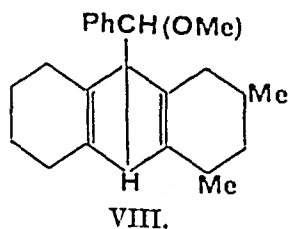
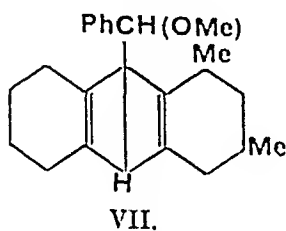
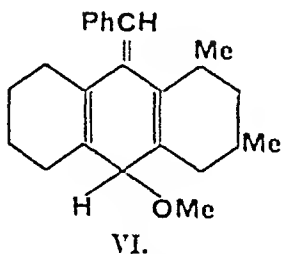
II.



Both of these hydrocarbons give monobromo-derivatives with very reactive bromine atoms, which must be either (IV) or (V), or a tautomeric mixture of the two.

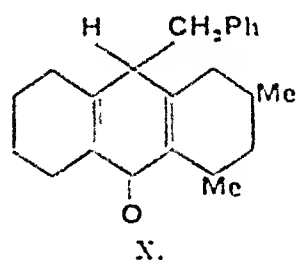
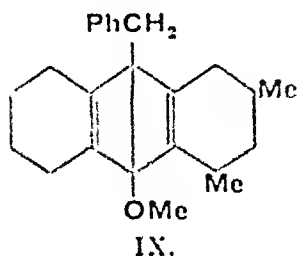


10-Bromo-1:3-dimethyl-9-benzylanthracene, (IV) or (V), with methyl alcohol and calcium carbonate, gives a methoxy-compound, colourless and free of fluorescence, hence of structure (VI). Its solutions in methanol show slight fluorescence, which becomes intense on heating with a trace of hydrochloric acid, but the new compound could not be obtained crystalline, and probably consists of the  $\omega$ -methoxy-compound (VII).



The bromo-compound from 2:4-dimethyl-9-benzylanthracene gave, by methanol treatment with or without calcium carbonate, a pale yellow, strongly fluorescent methoxy-compound (VIII), which is actually very stable to long heating with acetic-hydrochloric acid, and gives

no trace of the anthrone (X). Hence the other very unlikely possibility, 2:4-dimethyl-9-benzyl-10-methoxyanthracene, is ruled out (IX  $\rightarrow$  X).



The very different behaviour of the two bromo-compounds towards methanol can be explained on structural grounds, and must be ascribed to the ease with which the methoxy-group wanders in the one case (1:3-dimethyl) and not in the other (2:4-dimethyl).

Further research revealed a range of alkoxy-compounds with better crystallisation properties. 1:3- and 2:4-Dimethylanthrone brominate readily. Both bromoantrones readily react with aniline, dimethylaniline, and piperidine, giving compounds of the usual type. In this behaviour they differ from 10-bromoanthrone,<sup>107</sup> as do all the *Bz*-methyl-*ms*-bromoantrones so far prepared. The 1-methyl group in 10-bromo-1:3-dimethylanthrone enables a piperidine compound to be formed, in contrast to 10-bromo-3-methylanthrone, which gives bromodianthrone. Both the above piperidine derivatives were enolised with alcoholic alkali; they resemble 2:3-dimethyl compounds in this<sup>266</sup> and differ from the 1:4-dimethyl compounds, which with boiling alcoholic alkali, alone or with piperidine, are not enolised.<sup>265</sup>

Both bromoantrones react very smoothly with methanol in presence of calcium carbonate and give the methoxyantrones, resembling the 10-bromo-1:4- and 2:3-dimethylantrones in this respect. As expected, both methoxyantrones readily give the corresponding anthranil acetates with pyridine and acetic anhydride.

The Friedel-Crafts reaction with benzene on the two bromoantrones gives the corresponding phenylantrones, with the qualification that the 2:4-dimethyl-compound reacts smoothly with little tar formation, while the 1:3-compound gives much tar, and the yield of pure phenylanthrone does not exceed 15%. It is seen that 10-bromo-1:3-dimethylanthrone resembles bromoanthrone, while 10-bromo-2:4-dimethylanthrone is akin to the 1:4- and 2:3-dimethyl- and most of the  $\alpha$ -chloro-*ms*-bromoantrones discussed earlier. In addition 1:3- and 2:4-dimethyl-10-phenylantrones readily give the anthranil acetates, thus resembling the 2:3-

dimethyl-, and differing from the 1:4-dimethyl-10-phenylanthrone.

2:4-Dimethyl-10-phenylanthrone yields a well-defined crystalline hydrocarbon by Friedel-Crafts reaction with benzyl magnesium chloride and dehydration of the dihydroanthranol. It is yellow and fluorescent and hence is the benzyl-phenyldimethylantracene and not a benzyldiene compound. The corresponding 1:3-dimethyl compound fails to crystallise, but is intensely fluorescent and hence is probably also of the anthracene form. Similar results are obtained with methyl magnesium iodide, giving the 1:3:9- and 2:4:9-trimethyl-10-phenyl anthracenes.

Thus most of the abnormalities found in the 1:4-dimethyl series are absent in both 1:3- and 2:4-dimethyl series; the investigation of the 2- and 3-methyl- and the 2:3-dimethyl-compounds makes it very improbable that there is any restraining influence due to a methyl group in the  $\beta$ -position.

**Influence of Bz-Chloro- and Methyl Substituents.**—A comparison of 2:3-dichloro-10-bromoanthrone with 2:3-dimethyl-10-bromoanthrone confirms the slighter effect of chlorine atoms compared with methyl groups. Thus the dimethyl compound readily yields the dimethylaminophenylanthrone and the piperidinoanthrone, while the dichloro-, although it gives a dimethylaminophenylanthrone, yields dianthraquinone by the action of piperidine.<sup>270</sup>

The 2-chloro- and 2:3-dichloro-10-dimethylaminophenylanthrones both have deep green solutions in hot indifferent solvents, the colour being discharged on cooling; this effect is absent in the 3-chloro-derivative. The effect, usually attributed to presence of dianthraquinones, is not due to that cause here, as it is undiminished in low-boiling solvents in which dianthraquinone is insoluble.

2:3-Dichloro-10-bromoanthrone gives by the usual method 2:3-dichloro-10-phenylanthrone, which easily acetylates to the 9-anthranyl acetate. In contrast to the corresponding 1:4- and 1:5-dichloro-derivatives, all give the anthranyl acetates<sup>228a</sup> and none give anthranyl methyl ethers. 1:4-Dimethyl-10-phenylanthrone, however, cannot be acetylated<sup>265</sup> the greater effect of the methyl group thus being shown. Both 1:4- and 1:5-dichloro-10-phenylanthrones give benzyldiene compounds with benzyl magnesium chloride and subsequent dehydration.

2:3-Dichloroanthrone, by alkylation with benzyl chloride and alkali, gives an excellent yield of the 10-benzylanthranyl-9-benzyl ether, and is thus distinguished from 2-chloro- and 3-chloro-anthrone, which give dibenzylanthrone.<sup>259</sup> and 1:4- and 1:5-dichloroanthrones, which give monobenzylanthrone.<sup>249, 259</sup>

The formation of a benzyl ether was not observed in any other case, although such compounds might be present in the usual tarry by-products obtained in such reactions.

2-Methoxy- and 3-methoxy-anthrone give the 10-bromo-derivatives, which yield dimethylaminophenylanthrones; neither gives piperidine compounds, but some 2-methoxyanthraquinone and 3:3'-dimethoxydianthraquinone are isolated in the respective cases.

5:8-Dichloro-1:4-dimethylantrone<sup>274</sup> has an aggregation of  $\alpha$ -substituents, but these do not prevent enolisation, as it gives a red colour with alcoholic alkali and easily gives the acetate, which is only feebly fluorescent. It is reduced with zinc and caustic potash to the anthracene, which is more sluggish in its reaction with bromine than 1:4-dichloroanthrone,<sup>237</sup> but forms a stable dibromide. The bromination of the anthrone gives the normal 10-bromoanthrone, which can be converted to the piperidine-, phenyl-, and methoxy-anthrone by the usual methods.

The strong restraining influence of the substituents on the *meso*-hydrogen atom is very marked in these compounds. Boiling for 3 hours with pyridine-acetic anhydride leaves them unchanged, and none gives any colour on heating alone with pyridine. The difference is particularly noted in the 10-phenyl derivatives, as 1:4-dichloro-10-phenylanthrone gives a red colour in these conditions and readily forms an acetate, whereas 1:4-dimethylantrone gives an orange colour but is not acetylated.<sup>265</sup>

5:8-Dichloro-1:4-dimethylantrone reacts especially easily with benzyl chloride and caustic potash, giving the 10-benzyl compound, which, as expected, shows no tendency to enolise.

The investigations were completed by the examination of 2:4- and 1:3-dichloroanthrone, 2:3:6:7-tetrachloranthrone, 6:7-dichloro-2:3-dimethylantrone, and 2:3:6:7-tetramethylantrone, but the yield of the tetrachloro-derivative by reduction of the corresponding anthraquinone was so small as practically to exclude it from the investigation.<sup>277</sup>

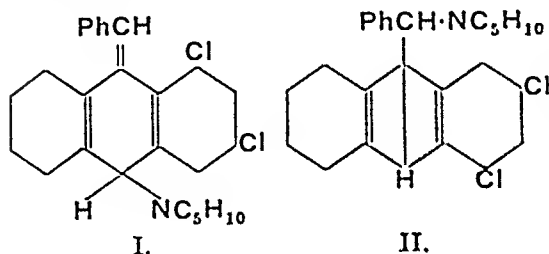
The 2:4- and 1:3-dichloroanthrones both give 10-bromo-compounds, which yield the anilido-derivatives with aniline, but are distinct in their behaviour with piperidine. Whereas the 2:4-dichloro-10-bromoanthrone gives a well-defined piperidino-derivative, the 1:3-dichloro-10-bromoanthrone easily yields the corresponding bromo-dianthranyl.<sup>199</sup>

The 4-chlorine atom also shows its influence on the behaviour to benzene in the Friedel-Crafts reaction: the 2:4-readily gives 2:4-dichloro-10-phenylanthrone, while the 1:3-gives only tarry products. In the benzyl chloride alkylation with caustic potash, the 1:3-dichloroanthrone gives a dibenzyl compound in good yield, thus resembling anthrone itself; the 2:4-compound only gives tarry products.

By the Grignard method with benzyl magnesium chloride and dehydration of the dihydroanthranols, both dichlorobenzylanthrone are obtained. These, by bromination, yield bromo-derivatives with reactive bromine atoms, which probably consist of a tautomeric mixture of the usual type.<sup>238, 251, 258a, 267</sup> The amount of the two tautomers present in the two cases is probably very different, for the 1:3-dichloro-compound gives a colourless (I), whereas the 2:4-dichloro-gives a yellow piperidine derivative (II).

The nitroanthrones obtained by nitration of the anthranyl acetates obey the rule that a nitroanthrone dissolved in pyridine can only be acetylated when no chlorine atom is present in the position *peri* to the nitro-group.

6:7-Dichloro-2:3-dimethylanthrone, by the Grignard reaction with benzyl magnesium chloride and dehydration, easily gives 6:7-dichloro-9-benzyl-2:3-dimethylanthrane, which is readily brominated to a yellow fluorescent monobromo-derivative, and is therefore 6:7-dichloro-10-bromo-9-benzyl-2:3-dimethylanthrane.



Remembering that 2:3-dimethylanthrone with benzyl chloride and caustic potash gives the 10:10-dibenzyl derivative,<sup>275</sup> whereas 2:3-dichloroanthrone gives the benzylanthranol benzyl ether,<sup>276</sup> it is found that both such reactions can occur with 6:7-dichloro-2:3-dimethylanthrone, and both have been described.

2:3:6:7-Tetramethylanthrone (the source of this is the corresponding tetramethylantraquinone of Morgan and Coulson),<sup>271</sup> gives no acetate by the usual method (pyridine-acetic anhydride), according to these authors, but it is found that when the anthrone is prepared by aluminium reduction of the tetramethylantraquinone, it gives a normal acetate. Benzyl chloride and alkali give the 10:10-dibenzyl derivative; benzyl magnesium chloride and dehydration give 2:3:6:7-tetramethyl-9-benzyl anthracene which yields a fluorescent 10-monobromo-derivative, the bromine being unreactive.

Of the sixteen derivatives of 9-benzylanthracene, containing one or more methyl groups or chlorine atoms, investigated by Barnett and his school, there are only six which, like 9-benzylanthracene, give on bromination a normal 10-bromo-compound as a single substance. These have no substituent in any  $\alpha$ -position. The other ten derivatives give bromo-compounds with reactive bromine atoms, although 1-chloro-9-benzylanthracene gives at the same time 1-chloro-10-bromo-9-benzylanthracene. The structure of the bromination product of a *ms*-benzylanthracene seems to depend on the position of the substituents in the side rings,  $\alpha$ -substituents, whether in the *peri*-position to the benzyl group or to the *ms*-hydrogen, leading to compounds with active bromine atoms.

### Bz-METHYLANTHRACENES.

The Bz-methyl anthracenes can be prepared by six methods. These are as follows:

1. Friedel-Crafts reactions between homologues of benzene and halogenated paraffins, e.g., methylene chloride.
2. Dehydration by long heating of homologues of phenyl *o*-tolyl ketones.
3. Pyrolysis of homologues of *o*-benzyltoluenes.
4. Reduction of anthraquinone homologues.
5. Zinc-distillation of homologues of *o*-benzoylbenzoic acid.

6. Certain special methods, e.g., Dewar and Jones's syntheses from benzene homologues with nickel tetracarbonyl and aluminium chloride, and Limprieth's heating of benzyl chloride and water under pressure (Annalen, 1868, 139, 307), which suggested Van Dorp's similar experiments with xylol chloride and water.<sup>3</sup>

These methods are now discussed in more detail.

1. *Friedel-Crafts Syntheses*.—These are mostly carried out with methylene chloride,<sup>23</sup> chloroform,<sup>21, 27</sup> tetrabromethane,<sup>42</sup> ethyldene chloride<sup>22</sup> and some  $\alpha$ -halogenated benzene homologues. The difficulties of the method lie in the orientation of the products. Their constitution must be checked by tedious methods, and the dubiety arises in two ways. Firstly, the benzene homologues can usually react in more than one way, and secondly, there is ample evidence that aluminium chloride in practice favours the migration of methyl or other groups, often in unforeseen ways. Examples are those described by Lavauz,<sup>160</sup> who, from di-*p*-tolylmethane and methylene chloride, which can only react together in one way, obtained a mixture of two dimethylanthraces, instead of pure 2:7-dimethylanthrane. The migration of a methyl group is the only possible explanation. This occurs in nearly every case where aluminium chloride is used.

2. *Dehydration of Phenyl o-Tolyl Ketones*.—Although the constitutions of the starting materials in this method are known, the temperatures used are so high that methyl migration is probable; consequently the orientation of the product must always be established independently, and this is a difficult problem.<sup>22, 24, 274</sup>

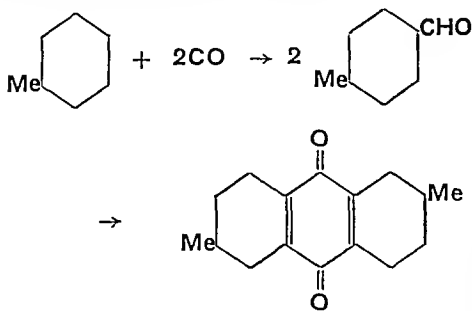
*Pyrolysis of o-Benzyltoluenes*.—Pyrolysis of many naturally occurring aromatic substances (e.g. di-*p*-tolylmethane and benzylmesitylene) yields not anthracenes but methylanthraces. The method suffers from the high temperature employed, which gives rise to splitting out and migration of groups.

3. *Reduction of Anthraquinones*.—Zinc distillation utilises high temperatures, and methyl groups are sometimes split off, so that mixtures are obtained containing anthracene. Thus Birukoff<sup>52</sup> obtained only impure 1-methylanthracene by zinc distillation of 1-methyl-4-hydroxyanthraquinone, the product containing anthracene.<sup>162</sup> The zinc-ammonia reduction developed by von Perger is more satisfactory, and in several cases gives excellent results in this field. The numerous dihydroanthranols which are intermediate products in this reaction do not all readily lose water to form the anthracene derivatives. Elbs<sup>53, 63</sup> described new reduction products, homologues of anthracene, which he considered contained a 1:9-four-membered ring ("anthracelyenes"), but von Braun and Bayer<sup>229</sup> showed that such compounds do not exist and that von Perger's method converts all methyl- and dimethyl-anthraquinones into anthracene homologues.

5. *Zinc Distillation of o-Benzoylbenzoic Acids*.—The same remarks apply as in the zinc distil-

lation of anthraquinone homologues, but the method has not been widely developed.<sup>45</sup>

6. *Special Methods*.—The uncertainty in the constitution of the Friedel-Crafts condensation products applies here also. Limpricht described the first synthesis of anthracene and its homologues. Dewar and Jones's reaction has not been completely clarified and the products are impure mixtures.<sup>108</sup> They suggest that aldehydes are formed as intermediate products, yet the pure aldehydes do not yield anthracene derivatives with aluminium chloride:



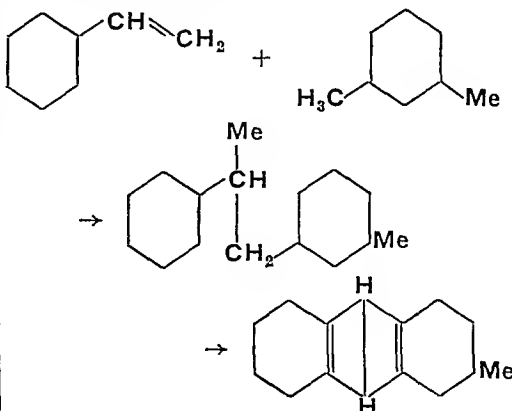
### Monomethylantracenes.

1. *Methylanthracene*.—Birukoff<sup>52</sup> and later C. Fischer and Sapper,<sup>162</sup> by zinc distillation of 1-methyl-4-hydroxyanthraquinone, obtained an impure hydrocarbon, mostly anthracene; 1-methyl-4-chloranthraquinone was shown to give better results, the methyl group being more stable. Then von Braun and Bayer, by ammonia-zinc reduction of 1-methylantraquinone<sup>229</sup> obtained it in a pure condition, and so disposed of Elbs' suggestion that the reduction product of 1-methylantraquinone by this method was a cyclic compound ("anthracyclene"). They also showed that the intermediate 1-methyl-9:10-dihydroanthranol was stable at 100°C. and was easily converted by distillation to the desired 1-methylanthracene. The m.p. of 1-methyl-anthracene is much lower than that of the 2-methyl (207°), in fact all α-methylantracenes melt below 100°C. This phenomenon is also found in the naphthalene series (naphthalene 79°, 2-methyl- 32.5°, 1-methyl- -20°).

1-Methylanthracene in sunlight readily yields a dimer, reconverted to the monomer at the melting point<sup>170</sup>; it also yields an addition compound with 2:7-dinitroanthraquinone consisting of orange-red crystals, m.p. 259°.<sup>230</sup>

2-Methylanthracene is rarely found in coal tar<sup>10, 12, 125</sup> and is indeed very undesirable in alizarine manufacture. It is not present in low-temperature tar<sup>235</sup> nor in turpentine tar,<sup>9</sup> but is obtained by zinc distillation from several natural products, such as chrysarobin,<sup>23, 95</sup> chrysophanic acid,<sup>66, 7</sup> frangula emodin,<sup>7, 95, 138</sup> abietic acid, or colophony.<sup>14</sup> Zinc distillation of 2-methylhydroxyanthraquinones [e.g., 2-methylquinizarin<sup>13</sup> and 6-methylhystazarin<sup>89</sup>], obtained by the benzoylbenzoic acid route, gives 2-methylanthracene by eliminating the hydroxyl groups. It can be obtained by pyrolysis of di-*p*-tolylmethane<sup>4</sup> and αα-di-*p*-tolylethane.<sup>5</sup> Kraemer and Spilker pyrolysed β-phenyl-α-

tolylpropane (from *m*-xylene and styrene), which splits off methane and hydrogen and gives 2-methylanthracene<sup>63</sup>:



It is obtained in small yield (with some of the three different dimethylantracenes) by condensing toluene with methylene chloride, chloroform, or tetrabromoethane, and aluminium chloride.<sup>107, 119, 120a, 150a</sup> It is obtained in fair yield by Elbs' method<sup>34, 56</sup> of long continued boiling of homologues of phenyl *o*-tolyl ketone, in this case phenyl 2:5-dimethylphenyl ketone. Gresly obtained it from phthalic anhydride and toluene, which gave 4'-methylbenzophenone-2-carboxylic acid, which on heating with zinc was reduced and split off water to give 2-methylantraquinone.<sup>45</sup>

It is most conveniently prepared from 2-methylantraquinone (from phthalic anhydride, toluene, and aluminium chloride, followed by sulphuric acid for ring closure) by zinc-ammonia reduction,<sup>26</sup> but the quinone can also be reduced with zinc<sup>87</sup> or with hydriodic acid and phosphorus.<sup>189</sup>

Whereas anthracene is reduced to dihydroanthracene, 2-methylanthracene does not give a dihydride, and hydriodic acid-phosphorus only converts the quinone to the aromatic hydrocarbon.

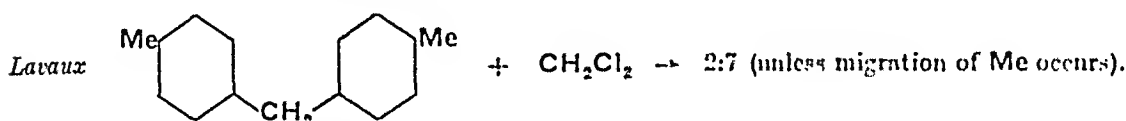
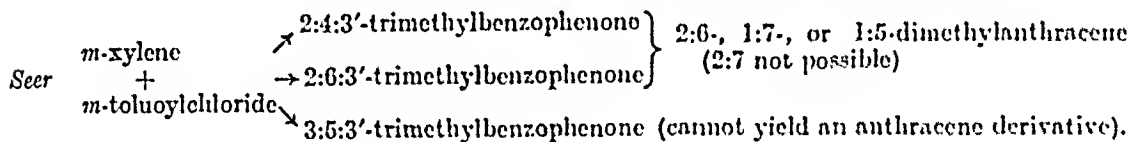
2-Methylanthracene yields a dimer in sunlight.<sup>86</sup> By oxidation with acetic-chromic acid, anthraquinone-2-carboxylic acid is obtained when excess oxidising agent is used; with theoretical amounts or with nitric acid in alcohol solution the oxidation stops at 2-methylantraquinone. It gives an addition compound with 2:7-dinitroanthraquinone, consisting of violet-green needles, m.p. 219°.

*Dimethylantracenes*.—Knowledge of the dimethylantracenes from the point of view of their constitution was for long scanty. Four homonuclear compounds are theoretically possible; these are known with fair certainty by reduction of the well-characterised dimethylantraquinones. Of the six possible heteronuclear compounds hardly one had been oriented with certainty until 1929.

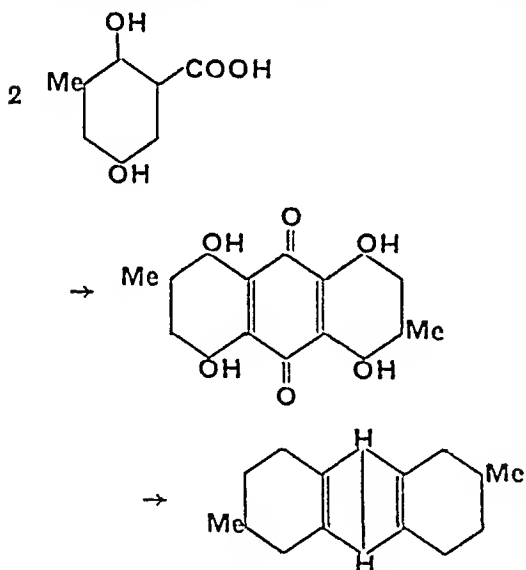
The Friedel-Crafts reaction is the commonest method for the heteronuclear dimethylantracenes, the melting-points of the products following closely those of the corresponding quinones (about 225°).

Lavaux in a series of original papers<sup>107, 119, 120, 129, 139, 150a, 154, 160</sup> showed that all the early preparations consisted essentially of a eutectic mixture of two dimethylantracenes of m.p. 240° and 244.5°, with quinones of m.p. 169° and 236.5°, and a small amount of a third isomer; this isomer was almost absent from the reaction product of methylene chloride and toluene, and quite absent when tetrabromoethane and toluene were used. Anschütz<sup>39, 46a</sup>

and Seer,<sup>164</sup> by using toluene and ethyldene chloride, in the one case, and the dehydration of 2:4:3'-trimethylbenzophenone in the other, obtained dimethylantracenes of m.p. 243-244°, with quinones of m.p. 235-236°, which are almost pure substances. Lavaux also found that di-*p*-tolylmethane and methylene chloride gives the mixed hydrocarbons, although theoretically it should give only a single hydrocarbon, which must be 2:7-dimethyl anthracene:



Seer's hydrocarbon was subsequently shown by Flumiani<sup>218</sup> to be identical with that obtained by the action of sulphuric acid on 2:5-dihydroxy-3-methylbenzoic acid, the resulting

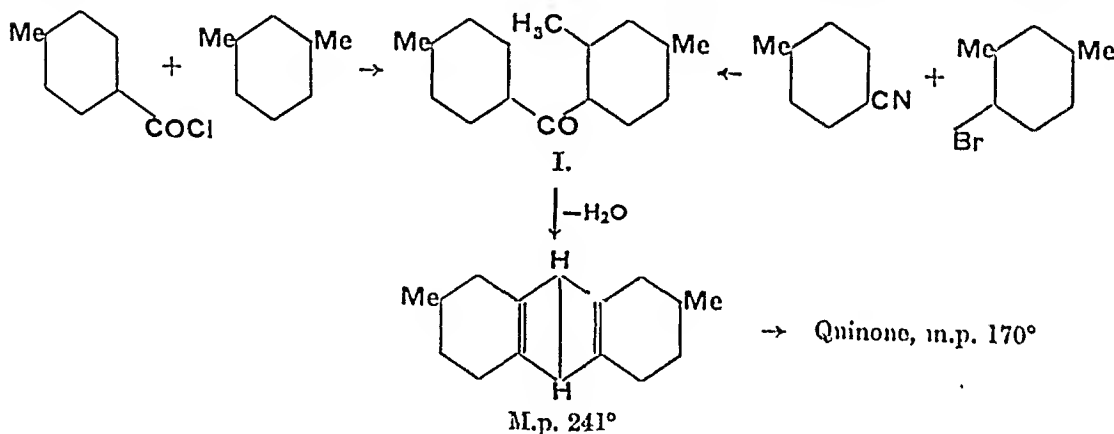


tetrahydroxydimethylantraquinone being reduced by zinc distillation to the dimethylantracene. This could only be the 2:6-dimethyl-compound.

While Lavaux considered that the above hydrocarbon obtained by his ditolylmethane method was 2:7- or 2:6-, the other isomer from the eutectic mixtures was considered to be probably 1:6-dimethylantracene, a conclusion based on evidence from its destructive oxidation, but the whole field remained doubtful until Morgan and Coulson<sup>224a</sup> cleared the obscurities by several quite independent methods.

The intermediate 2:4:4'-trimethylbenzophenone (I), an oily ketone characterised by its oxime, can only dehydrate in one way by heat, giving 2:7-dimethylantracene, unless migration of a methyl group occurs. The intermediate was made in two ways, in bulk by the Friedel-Crafts reaction of *p*-tolyl chloride with *m*-xylene, and in small quantity by the completely unambiguous Grignard reaction between *p*-toluonitrile and the magnesium compound from 4-bromo-1:3-dimethylbenzene, which yields a ketimine hydrolysing to the same ketone. This hydrocarbon is thus identical with Lavaux's supposed 1:6-compound<sup>150</sup> and is therefore 2:7-dimethylantracene.

Lavaux's other hydrocarbon, supposedly 2:7-, was shown to be identical with one prepared from 2:5:4'-trimethylbenzophenone (II) which again can only dehydrate in one way, to give the 2:6-dimethylantracene; the ketone was prepared in bulk by Friedel-Crafts reaction of *p*-toluylchloride and *p*-xylene, and its consti-

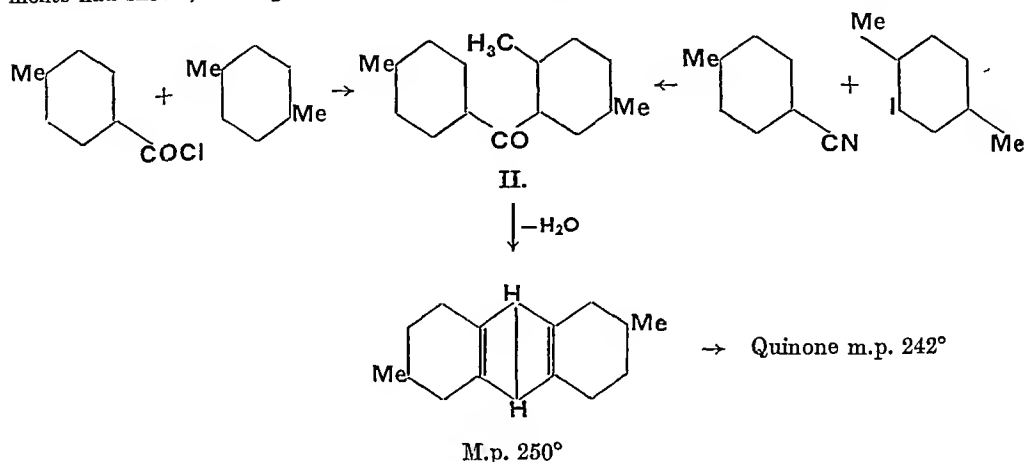




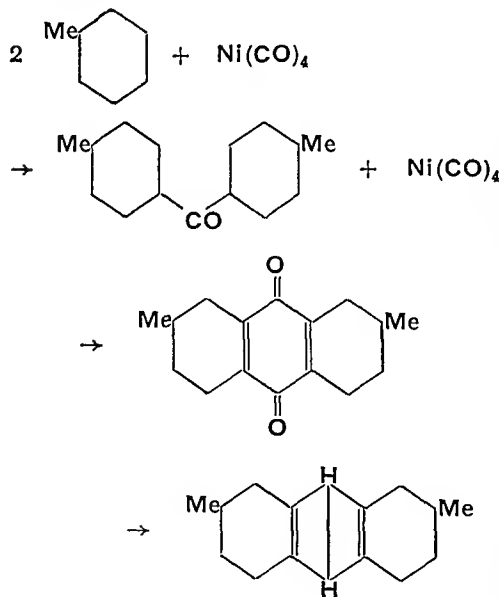
tution checked by an unambiguous Grignard method from *p*-toluonitrile and the magnesium compound from 2-iodo-*p*-xylene.

Thus Seer's compound was confirmed to be the 2:6-dimethyl, just as Flumiani's experiments had shown, although Seer's method was

open to two other mechanisms, but could not give the 2:7-dimethyl isomer. Lavaux's hydrocarbon, m.p. 240°, with its quinone of m.p. 169°, is thus 2:7-dimethylantracene, and that of m.p. 244·5°, with quinone m.p. 236·5°, is 2:6-dimethylantracene.



Dewar and Jones's<sup>108</sup> compound, obtained by the action of toluene on nickel tetracarbonyl, is also shown, as suspected by Seer, to be 2:7-dimethylantracene:



Morgan and Coulson also checked the condensation of di-*p*-tolylmethane with methylene chloride, studied by Lavaux, and confirmed that the 2:7-dimethylantracene predominates in the product. Lavaux's preparation must have suffered the migration of a methyl group, this migration accounting for the eutectic mixture he obtained.

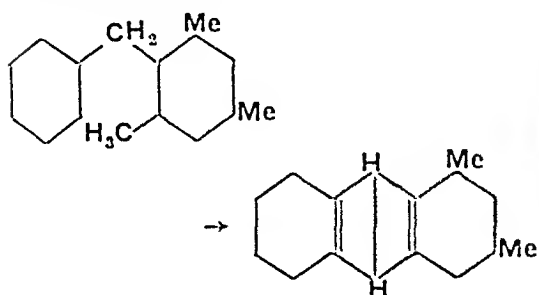
The other heteronuclear dimethylantracenes probably consist of mixtures.<sup>108</sup> R. D. Haworth and Sheldrick describe the 1:5-dimethyl-compound.<sup>280</sup>

The four homonuclear dimethylantracenes are prepared by zinc-ammonia reduction of the corresponding anthraquinones. Thus 2:3-dimethylantracene<sup>66</sup> was prepared from the 2:3-dimethylantracene arising by Friedel-Crafts reaction of phthalic anhydride with *o*-xylene, and dehydration. The structure of the dimethylbenzoylbenzoic acid was confirmed by F. Meyer,<sup>24</sup> yielding benzoic and 3:4-dimethylbenzoic acids. The ring-closure by dehydration can, and does,<sup>196</sup> give 1:2- or 2:3-dimethylantracene. The anthraquinone dicarboxylic acid prepared by oxidation, however,<sup>66</sup> is different from the 1:2-dicarboxylic acid, obtained by oxidising 1:2-benzanthraquinone,<sup>159</sup> but while Elbs and Eurich's dimethylantracene is certainly mainly the 2:3-dimethyl, it is contaminated by some 1:2-dimethyl-compound. An unambiguous route to 1:2-dimethylantracene is to treat the Grignard compound from 3-bromo-*o*-xylene with phthalic anhydride, giving 2-(2':3'-dimethylbenzoyl) benzoic acid. The latter can yield only 1:2-dimethylantracene on ring-closure, which may be carried out with benzoyl chloride and a little sulphuric acid,<sup>297</sup> or the ketonic acid may be reduced, and the dimethylbenzylbenzoic acid converted into the corresponding anthrone with zinc chloride in acetic acid.<sup>293</sup> 1:3- and 1:4-Dimethylantracenes were first prepared by von Braun and Bayer<sup>229</sup> from the quinones by zinc-ammonia reduction, Elbs having only impure material, which he named "anthracyclenes."<sup>67a</sup> The quinones from which the 1:3- and 1:4-dimethylantracenes were prepared are of certain constitution. Gresley<sup>45</sup> and Heller<sup>151</sup> obtained the 1:4-dimethylantracene by condensing *p*-xylene with phthalic anhydride; *m*-xylene gave the 1:3-dimethyl-compound in an equally certain manner.

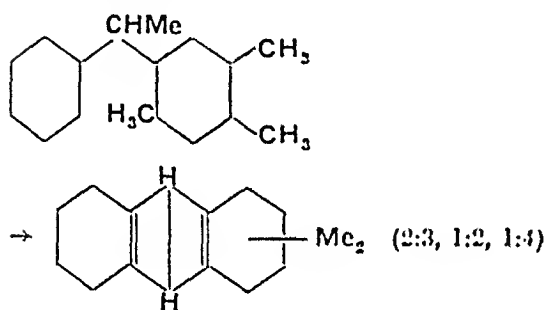
The pyrolysis product from benzylmesitylene, obtained by Louise,<sup>36, 43</sup> is probably an impure 1:3-dimethylantracene, as it corresponds with



that by the Friedel-Crafts route from mesitylene and phthalic anhydride:

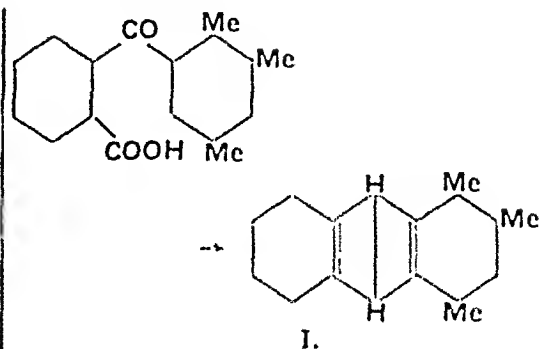


Kraemer, Spilker, and Eberhardt's pyrolysis of  $\alpha$ -phenyl- $\alpha$ - $\psi$ -cumylethano<sup>65</sup> is probably impure 2:3-dimethylantracene, although both 1:2-, 1:4-dimethylantracenes can arise in this way:

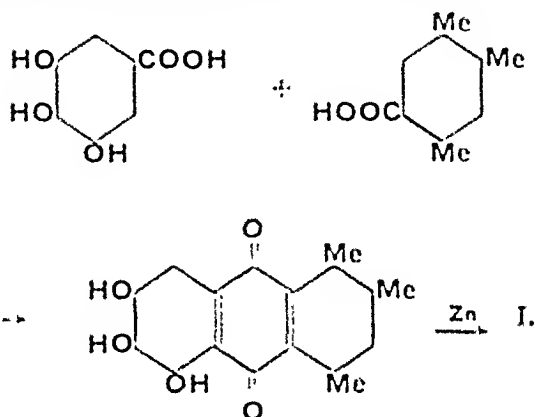


Other contradictory statements are given in the literature.<sup>45, 52</sup>

**Trimethylantracenes.**—1:2:4-Trimethylantracene is known with fair certainty. It was prepared by Gresley<sup>45</sup> and Elbs<sup>47, 56, 67</sup> by Friedel-Crafts reaction of *pseudocymene* with phthalic anhydride and zinc distillation of the resulting trimethylbenzoylbenzoic acid.

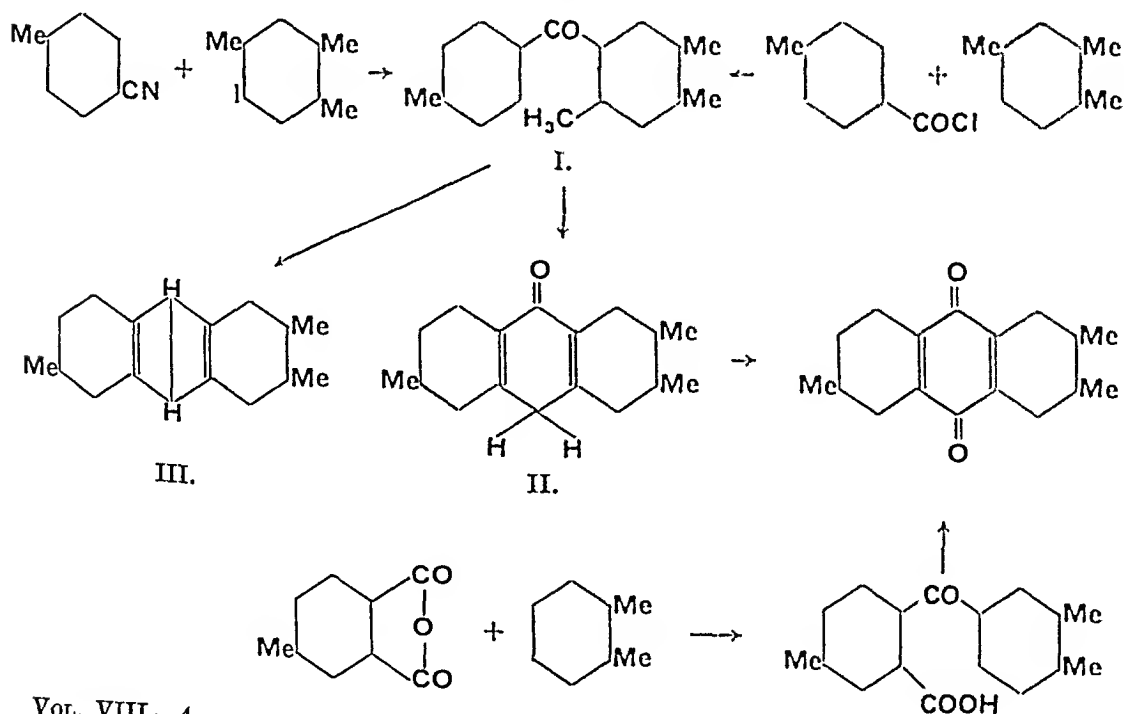


It was also obtained by Wende<sup>51</sup> by zinc distillation of trimethylantracagallol from the condensation of durylie and gallic acids:



1:3:6-Trimethylantracene, by long heating of 2:4:2':4', and 1:4:7-trimethylantracene, by the same method from 2:5:2':5'-tetramethylbenzophenone, were prepared by Elbs.<sup>47, 55, 67</sup>

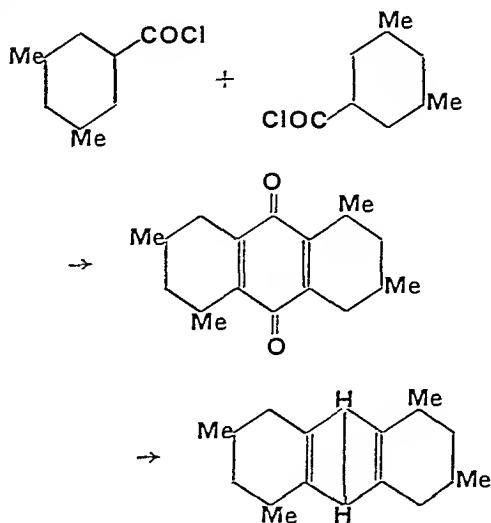
2:3:6-Trimethylantracene was synthesised by Morgan and Coulson,<sup>54</sup> by a method similar to that used for the 2:6- and 2:7-dimethylantracenes. 2:3:5:4'-Tetramethylbenzophenone (I),



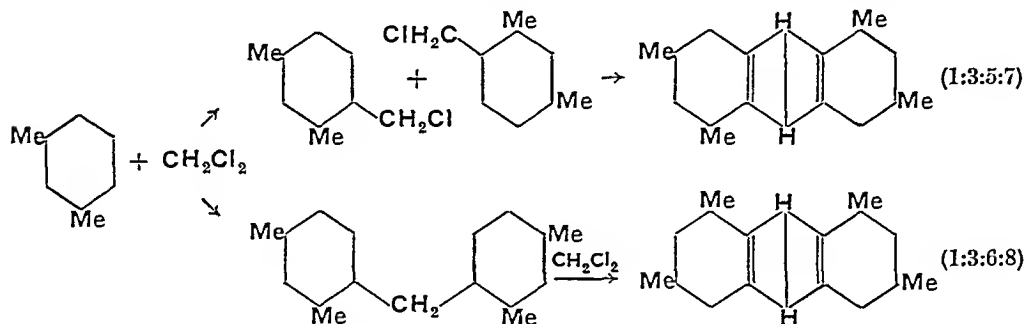
synthesised through the ketimine by Grignard reaction of *p*-toluonitrile with the magnesium compound of 5-iodo- $\psi$ -cumene to make its constitution certain, and identical with that prepared in quantity by Friedel-Crafts reaction of *p*-toluoylchloride with  $\psi$ -cumene, suffers on heating not the usual dehydration, but dehydrogenation to the anthrone (II), a reaction hitherto unknown for the *o*-methylbenzophenones. On longer boiling, however, water is eliminated in the normal manner, and 2:3:6-trimethylantracene, m.p. 255°, results; the corresponding quinone melts at 240°, and can be reduced to the pure trimethylantracene (III). The constitution was rendered doubly certain by synthesising a quinone, identical with that already obtained, by condensing 4-methylphthalic anhydride with *o*-xylene, and dehydrating the resulting trimethylphthaloylic acid, when the required trimethylantracenequinone is formed (although it is probably accompanied in smaller amounts by the other possible isomers, 1:2:6- and 1:2:7-).

**Tetramethylantracenes.**—1:3:5:7-Tetramethylantracene, obtained by Friedel and Crafts by interaction of *m*-xylene with methylene and aluminium chlorides,<sup>50</sup> was also obtained by Seer by zinc distillation of the quinone from mesitylenoyl chloride and aluminium chloride.<sup>171</sup>

The latter can give only a 1:3:5:7-tetramethyl derivative:

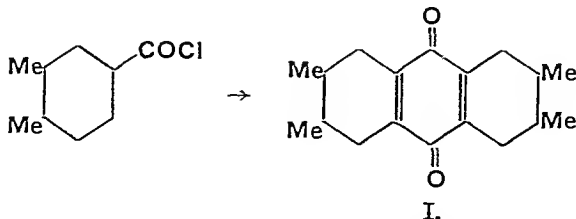


while the former can also give rise to the 1:3:6:8-compound which Seer obtained from a repetition of the Friedel-Crafts experiments:



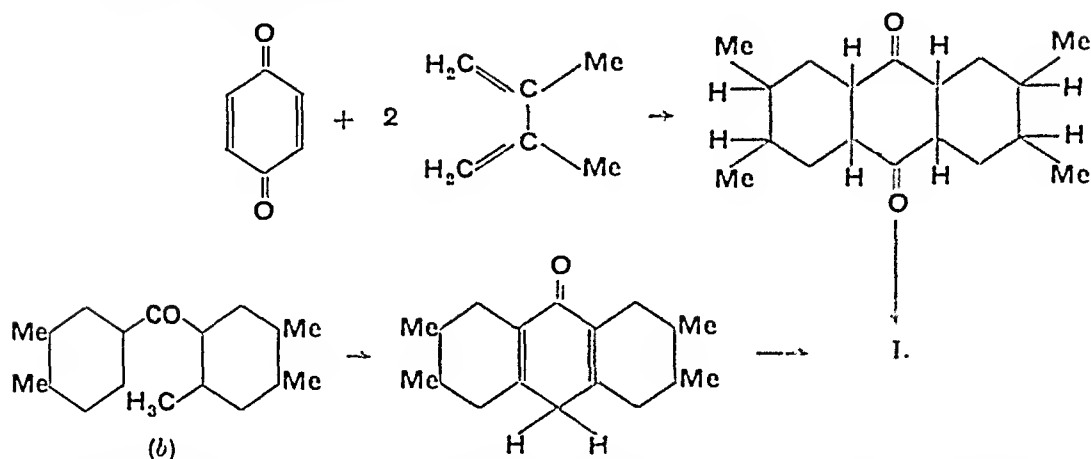
The 1:3:6:8-tetramethylantracene was also obtained by Anschütz from *m*-xylene, tetrabromoethane, and aluminium chloride,<sup>46a</sup> and is probably identical with Dewar and Jones's hydrocarbon obtained by using nickel tetracarbonyl in place of tetrabromoethane,<sup>103</sup> and is not the 1:3:5:7-tetramethyl-compound as these authors considered on untenable grounds.

The quinone (I) corresponding to 2:3:6:7-tetramethylantracene was prepared by Morgan and Coulson,<sup>271</sup> by Friedel-Crafts reaction of 3:4-dimethylbenzoylchloride (*a*) by itself, and (*b*) with  $\psi$ -cumene, to 2:4:5:3':4'-pentamethylbenzophenone, subsequently-pyrolysed to 2:3:6:7-tetramethyl-anthrone-9, which was oxidised to the quinone:



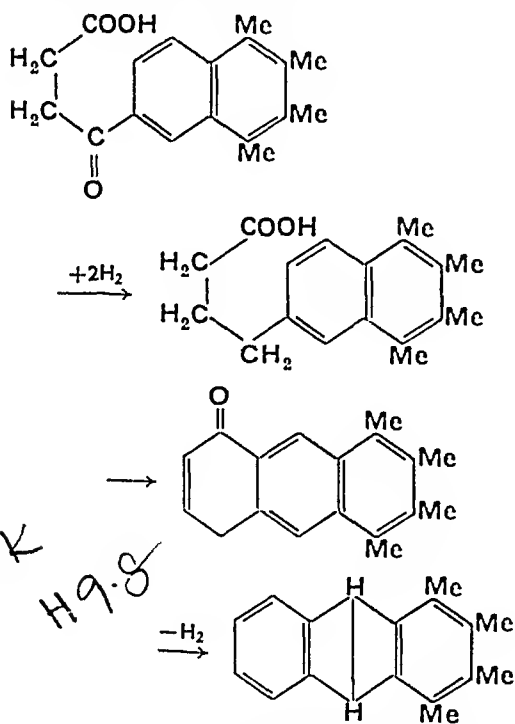
The anthracene prepared by reduction melted at 308°. Barnett, Goodway, and Watson<sup>277</sup> prepared a similar substance by the Friedel-Crafts methods from *o*-xylene and methylene chloride, which in a mixed melting-point determination with Morgan and Coulson's preparation melted at 299°, and so was not quite pure; it gave an an-

throne melting at 271°, identical with that quoted by Morgan and Coulson. The latter authors also prepared the quinone independently by the Diels-Alder method and mild oxidation, by condensing benzoquinone with  $\beta$ - $\gamma$ -dimethyl- $\Delta^{1:3}$ -butadiene to the octahydroanthraquinone and passing air into an alcohol solution of the latter.



The reduction of the quinone with sodium and amyl alcohol gave the tetramethyldihydroanthracene, dehydrogenated to the anthracene itself by selenium. The 2:3:6:7-tetramethylanthracene has been detected in the heavy neutral oils of low-temperature tar.

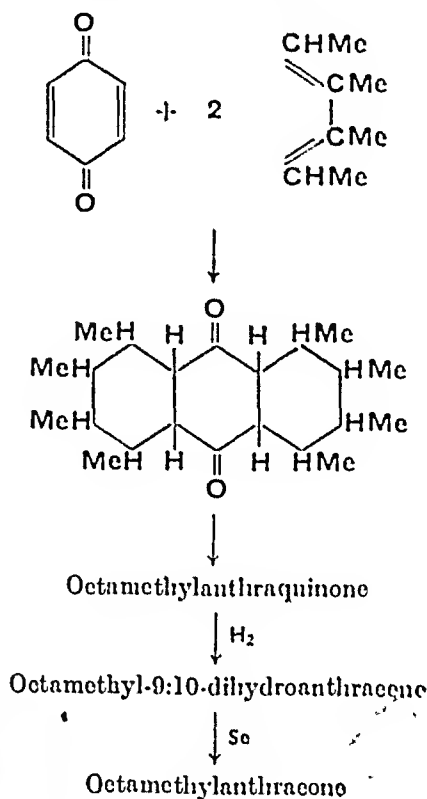
1:2:3:4-Tetramethylanthracene was obtained by Hewett<sup>291</sup> by chloromethylating 2:3-dimethylnaphthalene and removing the chlorine by reduction with hydrogen to give 1:2:3-trimethylnaphthalene. This process was repeated, giving 1:2:3:4-tetramethylnaphthalene. This, by reaction with succinic anhydride and aluminium chloride in nitrobenzene, gave  $\alpha$ -(1:2:3:4-tetramethyl-6-naphthoyl)-propionic acid, which was reduced to the tetramethylnaphthylbutyric acid, ring-closed to the ketotetrahydroanthracene, and dehydrogenated in two steps to 1:2:3:4-tetramethylanthracene.



When hydroquinone is condensed with diacetone in solution in acetic and sulphuric acids, two molecules of the  $\gamma$ -diketone react with the loss of four molecules of water, and the product simultaneously isomerises to 1:4:5:8-tetramethylanthraquinone.<sup>298</sup>

**Hexamethylanthracenes.**—*p*-Cymene, methylene chloride, and aluminium chloride yield a hexamethylanthracene which must be either 1:2:4:5:6:8- or 1:2:4:5:7:8-.<sup>29</sup>

**Octamethylanthracene.**—Backer, Strating, and Huisman<sup>294</sup> obtained the fully substituted octamethylanthracene by the Diels-Alder method, condensing benzoquinone with two molecules of tetramethylbutadiene to yield the adduct, the octamethyl octahydroanthraquinone. The latter is of course a mixture of many stereoisomers, but all yield the same octamethylanthraquinone on oxidation in a boiling butyl alcohol solution of caustic potash by passing in oxygen. The anthraquinone is stable to the classical zinc distillation method and even to hydriodic acid and phosphorus, but is reduced to the dihydroanthracene by Clemmensen's method with amalgamated zinc and hydrochloric acid; the latter is dehydrogenated by selenium in naphthalene solution to the octamethylanthracene, m.p. 283-284°.



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## ANTHRACENE CARBOXYLIC ACIDS.

Only the *mono-ms-carboxylic acid* is known, and this has already been discussed (p. 26c), under the action of acyl halides on anthracene. The *Bz*-acids can be obtained through the nitriles, which are saponified by means of alcoholic potash. The nitriles are prepared by distilling the corresponding alkali sulphonates with potassium cyanide or dry potassium ferrocyanide.

The 9-sulphonic acid is unknown, but the 9-nitrile can be prepared by Karrer and Zeller's method, by treating anthracene with fresh cyanogen bromide and aluminium chloride.<sup>194</sup> Again, Barnett, Cook, and Matthews converted 1:5-dichloranthracene-9:10-dibromide to 1:5-dichloranthracene-9-nitrile by heating with alcoholic potassium cyanide.<sup>225c</sup>

The main method for preparing anthracene carboxylic acids is zinc-ammonia reduction of the corresponding anthraquinone carboxylic acids, both di- and tri-carboxylic acids thus becoming available.<sup>30, 53, 66, 67, 80, 219, 263</sup>

The 1:9-dicarboxylic acid is obtained by regulated oxidation of aceanthrenequinone<sup>175</sup> and the action of dilute alkalis on the latter produces, among other products, some anthracene-1-aldehyde-9-carboxylic acid.

Whereas the 9-carboxylic acid readily decomposes on heating, giving off carbon dioxide, the *Bz*-acids are generally stable yellow substances which fluoresce blue in solution. Di- and tri-carboxylic acids with vicinal groups give orange-coloured anhydrides by sublimation,<sup>66, 67</sup> the 1:9-dicarboxylic acid doing so even in solution,<sup>175</sup> in which it resembles naphthalene-1:4:5:8-tetracarboxylic acid. The same acids also give yellow imides by the action of ammonia on the anhydrides, or from the oximes of the corresponding aceanthrenequinone by reaction with acids, and the imides or oximes yield leuco-vat dyes by alkali fusion, dyeing green shades from red vats (Aceanthrene Green).<sup>176</sup>

While the carboxylic acid groups can be split off by heating the alkaline-earth salts, the nitriles are very difficult to hydrolyse, the amides do not readily do so, and the acid chlorides are stable to water.<sup>30, 130</sup> The 9-carboxylic acid cannot be esterified by the normal method<sup>58</sup>; the methyl ester is prepared by heating the silver salt with methyl iodide, and is very stable to ammonia. The 1-carboxylamide does not undergo the Hofmann reaction.<sup>80</sup> All three monocarboxylic acids readily form dimers in light, but the 9-carboxylic acid is specially light-sensitive and must be kept in the dark *in vacuo*. The acids are oxidised to the corresponding anthraquinone carboxylic acids by chromium trioxide, the 9-carboxylic acid giving anthraquinone itself.

Whereas anthracene-2-carboxylic acid behaves like anthracene on bromination, giving only the 9:10-dibromo-derivative, the 1-carboxylic acid gives a *ms*-monobromo-derivative which cannot be further brominated, another example of the influence of the  $\alpha$ -substituent on the 9-peri-position.<sup>210</sup>

The 9:10-disulphonic acid can be prepared as

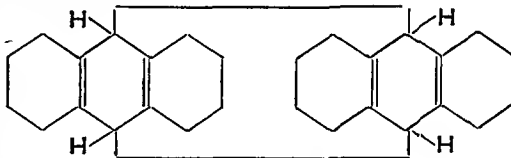
its disodium salt by heating 9:10-dichloranthracene with sodium sulphite in phenol solution at 170–180° (Marschalk, Ouroussov, Bull. Soc. chim. 1935, [v], 2, 1216.

## DIANTHRACENES.

The discovery of the dimers of anthracenes was due to Fritzsche (J. pr. Chem. 1867, [i], 101, 337; 1869, [i], 106, 274) who found that sunlight produced, in solutions of anthracenes in organic solvents, sparingly soluble substances with higher melting-points than the original monomers. They are decomposed to the monomers by melting. Elbs<sup>70</sup> determined their molecular weight by the cryoscopic method, supported by Orndorff and Cameron, by ebullioscopic methods,<sup>75</sup> both showing that the products were dimers. Linebarger determined the relative speed of formation in different solvents<sup>71</sup> but a solvent is not strictly necessary.

While 1- and 2-methylantracenes<sup>152</sup> readily dimerise,<sup>86</sup> and substituted derivatives, including the 9-halogeno-derivatives do likewise,<sup>170</sup> the 9:10-dihydro- and 9:10-dibromo-derivatives do not react at all, although this was disputed by H. Meyer and Eckert<sup>192</sup> in the case of dihydroanthracenes, which they found reacted in absence of air. As already referred to, all three monocarboxylic acids give dimers, but in the case of the 9-acid, air must be excluded as it causes the formation of anthraquinone.

The dimers are white solids, free of fluorescence; they do not form picrates, are very inert and have low solubilities. Linebarger's proposed constitution,



is so far without contradiction.<sup>71</sup>

ALKYLANTHRACENE DERIVATIVES  
FOUND IN NATURE.

A large number of hydroxyalkylantracene derivatives have been observed occurring in nature, sometimes free and in other cases as glucosides. These include:

- Aloe-emodin (v. Vol. I, 261b);
- Chrysarobin (v. Vol. III, 116b);
- Chrysophanic acid (v. Vol. I, 433a; II, 410d III, 116c);
- Emodin (v. Vol. III, 116c);
- Frangulin (v. Vol. V, 328d; VI, 88a);
- Frangula-emodin (v. Vol. V, 328d);
- Helminthosporin (v. Vol. V, 55a);
- Morindin (v. Vol. VI, 92a);
- Munjistin (v. Vol. V, 416b; VII, 437a);
- Rubiadin (v. Vol. V, 415d; VII, 437d).

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|      | 5 O. Fischer, <i>ibid.</i> 7, 1195,      |

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R. F. T.

## METHYLATED SPIRIT (v. Vol. I, 182d, 183a, b; III, 557d).

**METHYLAURIN.** Red dyestuff contained in crude aurin, which is prepared by heating phenol with sulphuric and oxalic acids. *Aurin*, a triphenylmethane derivative,  $C_{20}H_{16}O_3$ , also known as *rosolic acid*, is used for colouring lacquers, in the manufacture of photographic plates, and as an indicator in titration of acids with caustic alkalis.

J. N. G.

## METHYLDIPHENYLAMINE,



prepared by heating diphenylamine with dimethyl sulphate, is a pale yellow oil, b.p. 291–292°/760 mm., 145–145.5°/10 mm. *Chloroplatinate*, m.p. 207–209° (decomp.) (Gibson and Vining, J.C.S. 1923, 123, 835).

J. N. G.

## METHYLGLYOXAL (v. Vol. VII, 149b).

"METHYLHEXALIN" (v. Vol. VI, 226a).

METHYLHEXANONE (v. Vol. VII, 141d).

METHYLKETEN (v. Vol. VII, 104c).

METHYSTICUM (v. Vol. VII, 95d).

METMYOGLOBIN (v. Vol. VI, 166d).

**METOL**, *p*-Methylaminophenol sulphate. A photographic developer (Harger, J.S.C.I. 1919, 38, 234A; J. M. Eder, "Handbuch. der Photographie," 6te Aufl., Halle a.d. Saale, 1930, Vol. III, Pt. ii, p. 129). It forms crystals, which begin to char at 245° and melt with decomposition above 250°. Metol has been manufactured (Merck, G.P. 260234) by heating quinol with aqueous methylamine to 200° and neutralising the product with sulphuric acid (Ermen, J.S.C.I. 1923, 42, 522A). Metol prepared by Merck's process contains *p*-phenylenedimethylamine sulphate,



which is stated to be the cause of metol poisoning. For metol-eczema see Liesegang, A. 1939, III, 191. Alternative methods of manufacture are given in B.P. 132555; G.P. 205415. In analytical chemistry, metol is used as a reducing agent in the molybdate colorimetric method of determining phosphates.

J. N. G.

"METRAMINE" (v. Vol. I, 326a).

"METRAZOL" (v. Vol. VII, 276c).

**METTEGANG METHOD** (v. Vol. IV, 550c).

**METYCAINE**.  $\gamma$ -(2-Methylpiperidino)-propyl benzoate hydrochloride. Local anæsthetic (v. SYNTHETIC DRUGS).

S. E.

**MEXICAN BUCKEYE OIL** is contained in the seeds of *Ungnadia speciosa* (Fam. Sapindacæ), a shrub growing in Texas and Mexico. Cheel and Penfold (J.S.C.I. 1919, 38, 74r) give the following characteristics of the oil extracted by ether: yield 50%;  $\rho^{15}$  0.9117;  $n_D^{20}$  1.4666; iodine value 83.5; mean molecular weight of fatty acids, 288. The seeds contained sufficient of a cyanophoric glycoside to cause symptoms of poisoning during the analysis. According to Schnedler (Chem. Centr. 1889, II, 101), the oil contains olein 78%, and palmitin and stearin together 22%.

J. N. G.

**MIANIN** (v. Vol. I, 140a).

**MIARGYRITE**. Silver thioantimonite,  $\text{AgSbS}_2$ , occurring as small, usually indistinct, monoclinic crystals. These are black and opaque, with a metallic lustre, but thin splinters transmit a deep crimson colour; streak dark cherry-red;  $\rho$  5.2. Crystals were formerly found at Bräunsdorf, near Freiberg in Saxony, and compact masses of some size are met with in the silver mines of Bolivia.

L. J. S.

**MICA** (Ger. *Glimmer*). A group of minerals characterised by an excellent basal cleavage, enabling the natural crystals to be split into very thin sheets or films, commonly less than one-thousandth of an inch in thickness. The cleavage flakes are flexible and elastic through a very wide angle, and possess outstanding value as electrical insulators on account of their high dielectric strength and low thermal conductivity. The remarkable facility with which the minerals can be split is the result of an atomic structure based on continuous sheets of  $(\text{Si}, \text{Al})\text{O}_4$  tetra-

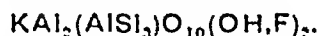
hedra, which are linked loosely through intervening potassium ions, cleavage being due to the rupture of the feeble potassium-oxygen bonds which hold the strong sheets together. Micas crystallise predominantly in the monoclinic system, with the  $\beta$  angle nearly 90°; crystals are usually tabular with prominent basal planes and pseudo-hexagonal habit, the prism faces being roughened by horizontal striations and often tapering. Although their hardness is only 2 to 3½, the flakes are strong;  $\rho$  2.7-3.2.

The micas form incomplete isomorphous series of sheet-structure minerals, consisting of complex aluminium silicates with potassium and hydroxyl, together with more or less magnesium, ferrous iron, and, in certain varieties, sodium, lithium, and ferric iron. Manganese, chromium, titanium, and vanadium are characteristic of some species, and fluorine is commonly present. The minerals may be classified chemically and structurally into two groups, the heptaphyllites and the octaphyllites; the former have seven positive ions, and the latter eight, accompanying twelve negative ions. No miscibility exists between the two groups.

The principal species, with their simplified formulae, are:

#### I. Heptaphyllites:

*Muscovite*, or potash-mica,

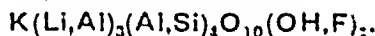


*Paragonite*, or soda-mica,

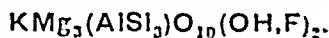


#### II. Octaphyllites:

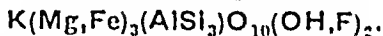
*Lepidolite*, or lithia-mica,



*Phlogopite*, or magnesia-mica,



*Biotite*, or ferromagnesian-mica,



Additional species are mentioned briefly below.

All the true micas yield water when strongly heated, the moisture content being about 5%; muscovite begins to lose water rapidly at 700°C., but phlogopite remains almost unaffected at temperatures below 1,000°C.

Muscovite frequently contains traces of ferrous and ferric iron, manganese, vanadium, etc. It is sometimes termed in the trade "white mica," though the crystals or "hooks" may be of a greenish, yellow, or reddish ("ruby") shade, which are transparent and almost colourless in thin films. Muscovite is a characteristic constituent of deep-seated siliceous igneous rocks, such as granite and syenite, and especially of certain pegmatite dykes; it is also widespread in many metamorphic schists and gneisses. The variety sericite, occurring as fibrous aggregates of minute scales with a silky lustre, tends to be rich in water, and is usually an alteration product of feldspar. Fuchsite, containing small amounts of chromium, has an attractive emerald green

colour; the crushed mineral is used in stucco and artificial stone, and polished fuchsite schist makes a handsome ornamental stone. Roscolite,  $KV_2(AlSi_3)O_{10}(OH)_2$ , is a clove-brown to greenish-brown variety in which aluminium is partly replaced by vanadium, with up to 29% of  $V_2O_5$ . It constitutes an important ore-mineral in the unique sedimentary uranium-vanadium-radium deposits of western Colorado, and is one of the chief economic vanadium minerals. The term ferri-muscovite is applied to muscovite which contains some ferric iron, and phengite refers to a variety containing magnesium and ferrous iron. Among the varieties often spoken of as hydro-micas are damourite and gilbertite, which are secondary forms occurring as minute scales and fibres with an unctuous feel and relatively poor elasticity. Paragonite, a yellowish or pale greenish mica, resembling muscovite in general properties, occurs as scales in certain metamorphic rocks of limited distribution.

Muscovite is employed in industry either as "sheet mica" or as "ground mica" made from mine waste or shop scrap. Most of the sheet mica is used as an insulating material in the manufacture of electrical apparatus, such as commutators, heating units (cookers, irons, and toasters), discs, washers, bushings, and condensers. A large quantity is used in the form of splittings or films bonded together with shellac or a special synthetic resin and heat-pressed into plates of required thickness, which are then shaped as desired into tubes, tape strips, V-rings, plates, and so on. This built-up mica is known in the trade as "*Micanite*." A certain amount of clear sheet muscovite, called "isinglass," finds employment in stove fronts, furnace and kiln windows, lamp canopies, chimneys, and shields, gas masks, goggle eye-pieces, etc. Wet-ground muscovite is used principally to impart lustre to wallpaper and some paints; it is also used to some extent as a filler in rubber and plastic compounds. The roofing industry absorbs a large proportion of the dry-ground mica produced, for use as a backing for rolled asphalt roofing and shingles, in order to prevent sticking, and for its decorative effect. This scrap mica adds finish to stucco, concrete, and artificial stone, is used for Christmas-tree "snow," and in axle-grease, as a dry lubricant, besides serving as a dusting and lubricating medium during the manufacture of tyres and other rubber goods.

Lepidolite is a comparatively rare lithia-mica, found in granitic pegmatite dykes, usually in association with other lithium-bearing minerals such as rubellite, tourmaline, amblygonite, and spodumene. Its composition varies considerably and includes the rare alkali-metals, rubidium and caesium, as normal constituents. One variety with considerable iron is called zinnwaldite, but protolithionite (approximately  $K_2LiFe_4Al_3Si_6O_{20}F_4$ ) contains still more. Another type with maximum lithium is polyolithionite,  $KLi_3AlSi_4O_{10}F_2$ . Lepidolite has a characteristic lilac-rose to violet-purple colour and is seldom found in large, clear sheets; it usually occurs in scaly, granular aggregates with a pearly lustre, often resembling granular lime-

stone. It colours the flame crimson and can thus be readily distinguished from pink muscovite.

Lepidolite and its varieties are important sources of lithium compounds (v. Vol. VII, 363c). Lepidolite is mainly used in its natural form in the glass industry for making special types of durable glass with a low coefficient of expansion, and it acts as an opacifier in opalescent white glass. It also serves to strengthen glass, glazes, enamels, and porcelains. The total annual world production of lepidolite, chiefly derived from California and New Mexico, is probably of the order of 1,000 tons.

Phlogopite is commonly yellowish-brown, often with copper- or bronze-red reflections from the cleavage flakes, though it is sometimes silvery grey, yellow, or green. According to the shade it is variously classified in the trade as dark amber, silver amber, wine amber, etc. It is transparent in thin sheets, and when viewed by transmitted light it frequently exhibits a starlike effect known as asterism. It is distinguished from muscovite by its decomposition in sulphuric acid, and from biotite by its lighter colour. With increasing iron it grades into biotite. Economic deposits of phlogopite are usually associated with basic igneous rocks, especially pyroxenites, which invade magnesian limestones. The phlogopite is commonly accompanied by apatite, and many of the Canadian deposits have been exploited for both their mica and their phosphate content. In common with muscovite its chief use is in electrical insulation, the best grades finding extensive service in heavy-duty spark plugs and commutators. Ground phlogopite is an ingredient of many moulded electrical insulators, in which it is bonded with various resins, rubbers, and cements.

Biotite is generally dark brown to black, though some varieties may be green or yellowish, the colour deepening to black in lepidomelane, in which there is much ferric iron. Biotite is a very common mica, being an important constituent of many igneous and metamorphic rocks, such as granite, syenite, diorite, gabbro, gneiss, and mica schist. It occurs in a wider variety of rocks than muscovite. Like dark phlogopite, biotite is of little value for electrical purposes owing to its low dielectric strength, but the powdered mineral, obtained by pulverising biotite schist, serves as a coating or filler material in the roofing and rubber trades.

Although not strictly a mica, it is appropriate to mention here the mica-like mineral vermiculite, a hydrothermal alteration product of biotite and phlogopite, which exfoliates and swells enormously on heating, and is now extensively employed for heat insulation and sound deadening.

Apart from the lithium and vanadium micas, the annual production of mica ranges from 30,000 to 50,000 tons, of which the United States produces about half, and the U.S.S.R. and India approximately 20% each. The American output is largely scrap and ground mica, whereas the muscovite deposits of Bihar and Madras in India normally supply about 90% of the world production of sheet mica for electrical insulation.



Canada and Madagascar are the principal sources of high-grade phlogopite.

*References.*—H. S. Speace, "Mica," Can. Dept. Mines Branch, No. 701, Ottawa, 1920; "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, New York, 1937, Chap. XXVI (comprehensive, with bibliography); R. H. Chowdhury, "Handbook of Mica," London, 1939; C. S. Fox, Rec. Geol. Survey India, 1935, 70, 247. During the past decade numerous articles dealing with the crystal structure and chemical composition of the various micas have appeared in volumes of the American Mineralogist, and complete references to mineralogical publications on mica are noted in successive volumes of Mineralogical Abstracts, issued by the Mineralogical Society, London.

D. W.

**MICELLE.** The micelle is the colloid unit in a certain class of colloidal solutions, often called micellar colloids, of which the best known examples are the soaps and synthetic detergents. The micelle is built up from molecules of crystalloidal size, and sols contain both molecularly and colloiddally dispersed solute in equilibrium according to the Law of Mass Action. If  $n$  molecules join together to form a micelle, its active mass will be given by the  $n$ th power of the concentration fraction, and, if  $K$  is the equilibrium constant,  $c$  the concentration of soap, and  $x$  the fraction aggregated, we have the relation:

$$K(cx/n) = \{c(1-x)\}^n$$

A small rise of molecular solubility of the soap, due to raising the temperature, will therefore be accompanied by a large increase in the amount colloiddally dispersed, and the overall solubility curve will become very steep at some point. This phenomenon is found in the soaps and similar long-chain synthetic detergents. The criterion for a substance to form micelles is that the molecule should be partly hydrophobic and partly polar and hydrophilic, the whole being large enough for the two properties to function separately. The simplest of these substances, which have been named "amphipathic," are long straight-chain hydrocarbons with a terminal polar group such as fatty acid, alkyl sulphate, sulphenate, amino, or amide. When the chain is sufficiently long, it is not carried into solution by the water-soluble end-group, and the hydrocarbon tails adhere to form the micelle with a hydrophilic exterior of the polar groups. The lower members of a homologous series form true solutions, while colloidal properties set in when the hydrocarbon tail has become long enough. For the ordinary sodium soaps, this occurs at  $C_8$  (caprylic acid). The majority of micellar colloids are also electrolytes, but not all colloidal electrolytes are micellar; e.g., the proteins do not fulfil the criterion that the single molecule should be of crystalloidal dimensions. The word "micelle" is not a synonym for a colloid particle or aggregate and its use should be restricted to systems which fulfil the criteria set out above.

The nature of solutions of micellar colloids was first clearly demonstrated by the classical researches of McBain,\* although his picture of

their composition has been altered in radical respects, largely owing to work carried out on solutions of the newer synthetic detergents, which are free from certain complications shown by the true soaps, probably owing to co-ordination effects in the  $\cdot\text{COOH}$  and  $\cdot\text{COOM}$  groups ( $M$  is a univalent metal). McBain measured electrical conductivities, osmotic pressures and hydroxyl ion concentrations; the results proved that the abnormally high conductivity of the more concentrated soap solutions was not due to hydrolysis, but accompanied micelle formation. In addition to the small amount of molecularly dispersed soap, neutral and ionic micelles were postulated as separate entities. It is generally accepted now that the neutral micelles do not exist. A very large amount of work has been carried out by a number of workers in the last 15 years, mainly on the long-chain alkyl sulphates and sulphonates, using electrical conductivity, transport number, and, less often, osmotic pressure measurements. Partial specific volume has also been used and, indeed, led Bury (J.C.S. 1929, 679) to the application of the Mass Action Law given above.

Surface tension measurements have played an important part. This property is due to the molecularly dispersed part of the soap, and therefore the onset of micelle formation is accompanied by a sharp break in the surface tension/concentration curve. The conditions for marked lowering of surface tension of water by soaps are the same as those for micelle formation, viz. a long hydrocarbon chain and a terminal polar group. The surface tension/concentration curve, like that of electrical conductivity, shows a steep initial fall, after which it bends round and then shows a small progressive rise. The concentration of soap required to reach the minimum is called the critical concentration. Its value is smallest for the least soluble soaps, and is increased by those factors which increase solubility, viz. increase of temperature, decrease of chain length, and choice of suitable polar end-groups or of the ions associated with them—the same factors, in fact, which determine the concentration at which micelle formation sets in. Considerable controversy has taken place over the point at which this does occur—at the critical concentration, or, as McBain originally suggested, at the higher concentration at which the steady rise begins. So far no decision has been possible, and perhaps the difference is not so real when it is considered that some sort of aggregation must set in at even the most extreme dilution. It is assumed, without adequate evidence, that the micelle is of a fixed size. Recent work on the examination of more concentrated soap/water systems by X-rays indicates that the soap is present in a layer lattice. In this case the conditions which have led to the idea of a spherical micelle, the size of which is determined by packing and charge distribution on its surface, no longer hold good, and there would be a wide range of micelle sizes. This would make the change of properties at the critical concentration less sharp than that given by the Mass Action relation,  $n$  being taken as 20 or a large value of that order.

\* The work of McBain and his co-workers is mainly published in J.C.S. from 1911 to 1927. A summary of this early work is found in the Third Report of The British Association on Colloid Chemistry, 1920, pp. 1-30.

Micelles can dissolve water-insoluble substances inside them. This was first regarded as solution in the hydrocarbon interior of the micelle but, in the more concentrated solutions of the potassium soaps, addition of oil is accompanied by increase of the long spacing of the soap lattice. Further experimental evidence is required, however, before the bearing of this result upon the nature of more dilute solutions can be decided. The nature and number of phases in more concentrated soap solutions is extremely complex and not yet fully understood.

*Bibliography.*—McBain's papers quoted above; G. S. Hartley, "Aqueous Solutions of Paraffin-chain Salts," 1936 (*Actualités Scientifiques et Industrielles*, No. 387); *Chem. Soc. Annual Rep.*, 1936, 110 (N. K. Adam); 1940, 99 (A. S. C. Lawrence); *Faraday Society Discussion on "Colloidal Electrolytes,"* Jan. 1935.

A. S. C. L.

**MICHAEL CONDENSATION** (*v. Vol. II, 367c; VI, 260a*).

**MICHAEL REACTION** (*v. VII, 476b*).

**MICHLER'S KETONE** (*v. Vol. VII, 131b*).

**MICRANTHINE** (*v. Vol. III, 547c*).

**MICROBALANCES** (*v. Vol. I, 607c*).

**MICROCHEMISTRY.** [This article is divided into three distinct sections, dealing with the use of "drop reactions" in inorganic qualitative analysis, selected microchemical manipulative methods, and organic micro-analysis, respectively.

Certain aspects of the use of drop reactions have been discussed in the article **CHEMICAL ANALYSIS** (*Vol. II, 579c*), and the additional information included below supplements this, and provides a review of a field which has developed rapidly since the original article was published.

The increasing use of micro-methods in organic chemistry has led to rapid development of new manipulative techniques, and to improvements in microanalytical methods, and these are described in the second and third sections of this article, which are again supplementary to parts of the article **CHEMICAL ANALYSIS** (*v. Vol. II, 629b*).—EDITORS.]

## DROP REACTIONS.

One of the most valuable results of the application of microchemical technique to practical chemistry has been the development of methods for detecting very small amounts of a substance, either alone or with other substances often present in relatively large amounts. Progress has been on two main lines, the one depending on the recognition of crystalline precipitates under the microscope, and the other on the formation of products of high visibility, usually the result of colour, when drops of solution react under suitably controlled conditions.

The first of these lines of progress, which for convenience can be referred to as the Behrens tests, was developed much before the other (P. D. C. Kley, "Behrens-Kley Mikrochemische Analyse," Leipzig and Hamburg, 1915; E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," J. Wiley and Sons, 1938), but made a greater appeal to the crystallographer and to the mineralogist than to the chemist, who, partly owing to the unfamiliar technique involved, made no serious use of the tests in his

analytical work. The second line of development, usually but unfortunately spoken of as "spot" tests, has, with its simpler and more trustworthy technique, made a wider appeal, and has now established itself, although tardily, as a part of the equipment of every modern analyst.

The term "drop reaction" includes both types of test, but there are clear indications that the second type will continue to be preferred, and except for a few Behrens tests which by their excellence deserve retention, this article will be confined almost entirely to drop reactions of the second type.

The characteristic feature of these tests is the formation of a coloured product by means of reagents usually organic in nature, and although some of the well-known reactions employing only inorganic reagents still hold their own, for example, the formation of permanganate ion as a test for manganese, future development rests mainly with the application of organic materials.

In order to provide a clearer and more definite picture of what these tests are really like, three examples will be described in some detail. The first, for copper, is carried out on filter-paper, the second, for zinc, in a small test-tube, and the third, for cobalt, in a micro-crucible, or in the depression of a white porcelain tile.

**Copper.**—A piece of filter-paper is moistened with a 1% alcoholic solution of dithioxamide (rubeanic acid), and allowed to dry. One drop\* of an ammoniacal solution containing copper is run from a glass capillary, of about the diameter of those used in an ordinary melting-point determination, on to the prepared paper. A black or greenish-black spot or ring, due to the complex rubeanate, indicates copper.

The test can be carried out in a different way. One drop of the practically neutral test-solution is added to filter-paper, which is then held over concentrated ammonia solution. One drop of the rubeanic acid solution is superimposed on that of the test solution. A black or greenish-black spot or ring indicates copper.

**Zinc.**—Three or four drops of the weakly acid or neutral test solution are placed in a small test-tube (approx.  $5 \times 1$  cm.), and one drop of copper sulphate solution, 0.1% with respect to cupric ions, is added, followed by ten drops of ammonium mercuric thiocyanate solution (80 g. of mercuric chloride and 90 g. of ammonium thiocyanate per litre). If no precipitate forms, the solution is boiled for one minute over a micro-flame, cooled, and then shaken with approximately one ml. of amyl acetate. A violet precipitate of the triple zinc copper mercuric thiocyanate, of a shade depending on conditions, collects at the interface of the two liquids to indicate zinc.

**Cobalt.**—One or two drops of the weakly acid test solution are placed in a micro-crucible, or in a depression of a white porcelain drop reaction plate. A crystal of ammonium thiocyanate, or five drops of a saturated solution of this substance in acetone, is added, and the whole stirred by means of a glass capillary sealed at one end. A greenish-blue or blue colour, due to the

\* Unless stated otherwise, in this article a drop should be taken as approximately 0.05 ml.

the product of reaction is confined to a smaller area than it would have been if the drop had been allowed to cover a larger area, as it does in the second procedure.

The slow addition of reagent or test solution to the paper is important, especially when a reaction is being employed near its limit, and in this same test adding the copper solution by means of a hair capillary is better than more rapid addition from a larger orifice. Greater time is thus allowed for the formation of the copper rubanate, and the black product appears as a small, intense spot which, if it had been allowed to disperse over a wider area, would have been much less definite, or even invisible.

The texture of the paper may be of importance. Thus in the test for cadmium with "cation" reagent (*see* p. 63a) the pink colour obtained is more easily seen when a No. 41 Whatman paper is used in preference to a No. 1, a No. 40, or No. 120, the special drop-reaction paper.

The area of a reaction can be confined also by means of a paraffin ring deposited in the fibres of the paper, to leave a clear space of known size in which the reaction can take place (H. Yagoda, *Ind. Eng. Chem. [Anal.]*, 1937, 9, 79; *Mikrochem.* 1938, 24, 117).

Impregnation of thin, close-textured papers with reagents of low solubility is another device that gives enhanced sensitivity, again by limiting the area of reaction. For example, a paper treated with zinc ferrocyanide instead of the more soluble potassium salt provides an improved test for ferric iron. The careful selection of less-soluble reagents for impregnating drop-reaction paper, combined with the use of capillaries to minimise spreading, has resulted in large increases in sensitivity for many familiar reactions (B. L. Clarke and H. W. Hermance, *Ind. Eng. Chem. [Anal.]*, 1937, 9, 292; 1938, 10, 591).

Extraction with an immiscible solvent may improve a test; thus, in the reaction described above for zinc, shaking the solution with amyl acetate collects the purple crystals at the interface between solution and organic liquid and makes them easier to see. This device has been recently applied by Korenman and co-workers in "flotational" reactions for nickel and palladium with dimethylglyoxime, aluminium with "aluminon," and bismuth with potassium iodide (*see* *J. Appl. Chem. Russia*, 1939, 12, 1742; 1941, 14, 669; 1940, 13, 309; 1939, 12, 1740).

The presence of salts accumulated during the preparation of a solution for testing, from, say, neutralisation of acids or alkalis, or from a fusion of insoluble substances with a flux, generally depresses sensitivity. In the above test for zinc, for example, excessive amounts of sodium salts should be avoided. There are also several instances known of the adverse effect of the presence of ammonium salts. The deliberate addition, too, of certain reagents necessary for preventing interference by other ions in a solution may have an unfavourable effect, and substances that are apparently quite indifferent can decrease sensitivity to a marked extent. Such substances, however, occasionally improve sensitivity. Thus, the detection of magnesium by

the well-known Titan Yellow test is more sensitive in presence of calcium salts which, by themselves, do not react (Kolthoff, *Chem. Weekblad*, 1927, 24, 254).

Examination of a solution in ultra-violet light (*cf.* Goté, *Sci. Rep. Tôhoku*, 1940, 29, 204, 287; *see also* J. A. Radley and J. Grant, "Fluorescence Analysis in Ultra-violet Light," London, 1939), as in the morin test for aluminium, effecting reaction in capillaries (Thomson, *Mikrochem.* 1937, 21, 209; *Mikrochim. Acta*, 1938, 2, 280), or on desilvered photographic paper (Korenman, *Mikrochem.*, 1936, 21, 17), and collecting traces of substances from solution by means of induced precipitation before applying a reaction (*see*, for example, Feigl and Rajmann, *ibid.* 1935, 19, 60, where traces of titanium are collected by co-precipitation with zirconium arsenate, and confirmed by the hydrogen peroxide reaction), are all methods that have been used to gain improved sensitivity.

Finally, it should be remembered that some of the organic reagents employed do not keep well in solution for long periods of time. They may easily lose much of their effectiveness as reagents, and it is a good rule to use freshly-prepared solutions from reagents of high quality when a reaction is being investigated for the first time, or is being used near its limiting conditions.

**Specific and Selective Reactions.**—Few of the drop reactions in use at the present time are specific in the sense that English-speaking people use the word, but in the past a good deal of misunderstanding has unfortunately arisen, partly owing to laxity in expression and a misapprehension of the implication of the term "spezifisch," which German-speaking authors use in a wider and different sense, and partly owing to insufficient data on, and investigation of, the scope of a test (*see* Theobald, *Chem. Soc. Annual Rep.* 1936, 33, 453; 1937, 34, 489). The position has been made clearer by a ruling of the International Committee on new Analytical Reactions and Reagents concerning the terms "specific" and "selective," and in view of the importance of using these terms correctly the recommendation is quoted at length. "The Committee . . . has decided to differentiate between *specific* and *selective* reactions (and reagents) and recommends this convention for general use. Reactions (and reagents), which under the experimental conditions employed are indicative of one substance (or ion) only, are designated as *specific*, whilst those reactions (and reagents) which are characteristic of a comparatively small number of substances are classified as *selective*. From this it follows that it is permissible to describe reactions (or reagents) as having varying degrees of selectivity; on the other hand a reaction (or reagent) can be only specific or not specific" (*see Analyst*, 1937, 62, 558; *Chem. and Ind.* 1937, 56, 535). It is desirable that this recommendation should be carefully followed, so that in the future false claims for a reaction and the discrediting of the test that this entails, will be avoided.

That the need for a fuller investigation of many tests and more experimental data concerning them is being realised and met is shown

by the critical examinations of certain reactions that appear from time to time (see, for example, Newell, Ficklen, and Maxfield, *Ind. Eng. Chem. [Anal.]*, 1935, 7, 26, on the encothelin test for tin; Ficklen, Newell, and Pike, *Z. anal. Chem.* 1936, 104, 30, on the cinchonine-potassium iodide reagent for bismuth; *idem*, *Z. anorg. Chem.* 1935, 225, 281, and Mehlig and Johnson, *Ind. Eng. Chem. [Anal.]*, 1940, 12, 30, on the *p*-nitrobenzenecarboresorcinol test for magnesium; Smith and West, *ibid.* 1941, 13, 271, and West, *J. Chem. Educ.* 1941, 18, 528, on interferences occurring with selected drop reactions; and a series of critical studies of qualitative reagents for cations—an extension of the work of the International Committee on Analytical Reagents—by Wenger and Duekert in *Helv. Chim. Acta*, 1941 onwards).

**Selectivity of Reactions.**—The selectivity as distinct from the sensitivity of a test can often be improved in various ways. For example, the test for copper with rubeanic acid can, within limits, be carried out in presence of nickel and cobalt by taking advantage of the capillary action of the paper used. Under suitable conditions, the black spot due to copper rubeanate and the purple and brown rings due, respectively, to the nickel and cobalt compounds are separated into distinct zones due, probably, to a combination of adsorption effects with different rates of diffusion and reaction of the nickel and cobalt in the paper. The same factors make reactions on paper more selective, in general, than those done in test-tubes, or in the depressions of a drop-reaction plate.

Treatment with an organic solvent may make drop reactions carried out in solution more selective, as in the triple thiocyanate test for zinc, where shaking with amyl acetate collects the purple crystals at the interface between the two liquids and gives both increased selectivity and sensitivity. Extraction methods are common, too, in reactions involving the use of dithizone.

The most important method of increasing selectivity is, however, effected by using the well-known device of adding fluoride, phosphate, citrate, tartrate, cyanides, etc., to "lock up" possible interfering substances as complex ions, which then no longer interfere with the reaction being used as a test. Thus, in the thiocyanate test for cobalt, interference by the red colour of ferric thiocyanate is prevented by adding fluoride to form with any iron present the complex  $[\text{FeF}_6]^{3-}$ , which does not react.

It must be remembered, however, that the use of these "masking" reagents generally involves a loss of sensitivity, and, in extreme cases, may cause a test to fail. To guard against the possibility of mistakes being made in the practical application of drop reactions to the varied problems of applied analysis, it is essential to check the validity of a test by means of controls. The possible adverse effect of the presence of masking reagents on the identification of a particular ion should always be ascertained by carrying out an additional test under conditions as similar as possible to those of the actual test, after the addition of a known amount of the ion being sought. Similarly, the possibility of a masking agent failing to perform

its expected function, owing to the presence of other substances in solution, should be checked by obtaining a satisfactory negative test in the known absence of the ion being sought. Fortunately, in dealing with reactions on a micro- or semi-micro scale this can easily be done, and the test proper and its controls can be run side by side with little additional effort and trouble.

Although much can be done by masking agents in the detection of a given ion to prevent interference by other ions that may be present, the addition of these reagents should not be regarded as an infallible means of avoiding a preliminary separation into groups. The desirability of making such a separation depends to a large extent on the nature of the substance under examination, and on the knowledge available concerning the known absence or likely presence of other substances in it. The tendency to make short cuts by avoiding a separation is fraught with danger, and is to be deprecated as fundamentally unsound. Group separations are still essential for the complete analysis of any but the simplest materials, and a judicious combination of these separations and drop reactions is probably the goal at which to aim in the qualitative analysis of the future.

**Technique and Apparatus.**—Technique is relatively simple, and requires only a certain neatness in manipulation, and scrupulous cleanliness. Apparatus, too, is simple, and easily made. The chief requirements are small test-tubes, a porcelain or glass plate with hemispherical depressions, small crucibles, glass capillaries drawn from tubing or old test tubes, glass droppers drawn out at one end to give drops, 0.03-0.05 ml. in volume, glass stirrers in the form of capillaries sealed at one end, a platinum wire with a loop of known size, unglazed porcelain rods for fusions, a micro-burner, good quality filter-paper, and a thicker type of paper (Whatman, No. 120) made specially for these reactions. A hand centrifuge is the most expensive piece of apparatus required, but much of the work can be done without it, and small filters of various types, easily made by a glass-blower of moderate skill, can be used instead. Special pieces of apparatus, still comparatively simple, for applying some tests in the most sensitive way are described in various textbooks on the subject. For the Behrens tests, a microscope of low power, preferably fitted with a polariser is, of course, essential. The more elaborate and exacting technique used in the analysis of 1  $\mu\text{g}$ . of solid material cannot be described here, and the original papers (A. A. Benedetti-Pichler, *Ind. Eng. Chem. [Anal.]*, 1937, 9, 483; 1942, 14, 813; "Introduction to the Microtechnique of Inorganic Analysis," John Wiley and Sons, 1942) must be consulted.

Many drop reactions, however, can with advantage be carried out quite simply on a semi-micro-scale without recourse to the more elaborate technique demanded by truly micro-procedures.

#### SELECTED DROP REACTIONS.

Serviceable drop reactions have already been described in other articles (see Vol. II, 579c, and articles on individual elements). The list that

follows has been compiled from the tests specially recommended by the International Committee on New Analytical Reactions and Reagents, and from the writer's necessarily limited experience of these reactions. No claim is made that a selected reaction is the best available; indeed, the tests for some elements are so numerous that such a claim would be unwise. Furthermore, some tests, although doubtless of value, have not come to the front owing to the difficulty of obtaining the necessary reagents, which are usually complex organic compounds not readily available; others involving organic reagents possess little or no advantage over a familiar, well-tried, and simpler reagent; for example, the thiocyanate test still holds its own as a qualitative reagent for ferric ions. Personal taste, practical experience, facilities to hand, and the nature of the problem to be solved, will determine the analyst's final choice.

## SELECTED DROP REACTIONS.

(The tests are described in the alphabetical order of symbols of the elements or groups to which they apply.)

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Ag	<i>p</i> -Dimethylamino-benzylidenerhodanine in acetone ("Rhodanine").	Reddish-violet precipitate or spot.	0.02 $\mu$ g./0.05 ml.	I.F.T.S.H.B.A. [See Wenger <i>et al.</i> , <i>Helv. Chim. Acta</i> , 1943, 26, 1465, for a critical study of reactions of Ag.]
Al	(a) $\text{NH}_4$ aurintricarboxylate ("aluminon").	Red lake or colour.	1 $\mu$ g./0.1 ml.	I.T.S.H.B.A.
	(b) Morin.	Green fluorescence.	0.13 $\mu$ g./0.03 ml.	I.T.F.
$\text{As}^{\text{III}}$	(a) Zn and NaOH.	$\text{AsH}_3$ evolved; gives black or brown spot with aq. $\text{AgNO}_3$ .	0.05 $\mu$ g./0.03 ml.*	
	(b) $\text{SnCl}_2$ in conc. HCl.	Brown to black precipitate.	2 $\mu$ g./0.1 ml.	I.T.F.
Au	(a) <i>p</i> -Dimethylaminobenzylidenesrhodanine.	Violet spot or ring.	0.06 $\mu$ g./0.03 ml.	I.F.T.H.
	(b) Pyridine and HBr.	Pleochroic rods or prisms.	0.02 $\mu$ g.	I.C. Putnam, <i>Amer. J. Sci.</i> , 1928, 15, 455.
Ba	Sodium rhodizonate.	Brown spot, turned red by dil. HCl.	0.14 $\mu$ g./0.03 ml.	I.F.T.S.B.A. [See Feigl and Suter, <i>Ind. Eng. Chem. [Anal.]</i> , 1942, 14, 840.]
Be	(a) Quinalizarin.	Blue colour.	0.08 $\mu$ g./0.03 ml.	I.T.F.H.B.A. [ <i>Cf.</i> White and Lowe, <i>ibid.</i> 1941, 13, 809, for a fluorescence reaction with 1-amino-4-hydroxyanthraquinone.]
	(b) Morin.	Yellow-green fluorescence.	0.6 $\mu$ g./0.03 ml.	I.
	(c) Acetic acid.	Crystals of basic beryllium acetate on sublimation.		[See Sandell, <i>ibid.</i> 1940, 12, 762. Benedetti-Pichler and Spikes, <i>Mikrochem.</i> 1937, 21, 268.]

\* Value obtained by the writer.

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Bi	(a) Cinchonine and KI.	Orange-red spot.	0.1 µg./0.03 ml.	I.T.F.B.A. [See Ficklen <i>et al.</i> , <i>Z. anal. Chem.</i> 1936, 104, 30.]
	(b) Thionrea.	Yellow colour.	6 µg./0.03 ml.	I.S.H.B. [Cf. Yoc and Overholser, <i>Ind. Eng. Chem. [Anal.]</i> , 1942, 14, 435.]
BO <sub>3</sub> '''	Turmeric, EtOH, salicylic acid, HCl.	Red colour → blue with aq. NH <sub>3</sub> .	0.02 µg.	Michel, <i>Mikrochem.</i> 1941, 29, 63.
Br'	(a) PbO <sub>2</sub> and AcOH or Chromic acid.	Bromine evolved to give red colour with fluorescein.	2 µg./0.05 ml.	I.F.T.B.A.
	(b) Chromic acid.	Bromine evolved to restore the colour of fuchsin decolorised by SO <sub>2</sub> .	3.2 µg./0.05 ml.	I.F.T.
Ca	(a) Oszone of dihydroxy - tartaric acid.	Yellow precipitate.	0.01 µg./0.03 ml.	I.T.F.H.B.
	(b) Ammonium ferrocyanide.	White precipitate.	25 µg./0.05 ml.	F.T.C.
Cd	(a) <i>p</i> - Nitrodiazo - aminoazobenzene ("Cation") and NaOH.	Pink spot.	0.01 µg./0.02 ml.	Dwyer, <i>J. Proc. Austral. Chem. Inst.</i> 1937, 4, 26.
	(b) 4 - Nitronaphthalenediazoaminoazobenzene-4' - azobenzene ("Cation 2 B").	Red colour.	0.002 µg./0.0125 ml.	H. B. Dwyer, <i>ibid.</i> 1938, 5, 37.
Ce	Hydrogen peroxide and aq. ammonia.	Yellow-orange precipitate.	0.35 µg./0.05 ml.	I.T.F. [See Wenger <i>et al.</i> , <i>Helv. Chim. Acta</i> , 1942, 25, 1547, for a critical study of reactions for Ce; and <i>idem</i> , <i>ibid.</i> , 1944, 27, 1479, for a reaction with <i>p</i> -phenetidine.]
Cl'	Solid potassium dichromate, concentrated H <sub>2</sub> SO <sub>4</sub> .	Chromyl chloride evolved and detected as chromate by the violet colour obtained with diphenylcarb. azide.	3 µg./0.01 ml.	I.F.T.
Co	(a) α - Nitroso - β - naphthol.	Red precipitate or colour.	0.01 µg./0.01 ml.	I.T.F.S.H.B.A.
	(b) Ammonium thiocyanate (solid, or in acetone).	Blue colour.	0.5 µg./0.05 ml.	T.I.F.S. [See Wenger <i>et al.</i> , <i>ibid.</i> 1941, 24, 657, for critical study of reactions of Co <sup>++</sup> .]

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
$\text{CO}_3''$	Dilute sulphuric acid.	$\text{CO}_2$ evolved, and sodium carbonate solution, coloured red by phenolphthalein, decolorised.	4 $\mu\text{g.}/0.05 \text{ ml.}$	I.F.
Cr ( $\text{Cr}_2\text{O}_7''$ )	(a) $\text{H}_2\text{O}_2$ in weakly acid solution. (b) Diphenylcarb-azide.	Blue colour. Violet colour.	0.5 $\mu\text{g.}/0.03 \text{ ml.}^*$ 10 $\mu\text{g.}/5 \text{ ml.}$	I.T. I.F.T.S.H.B.A.
Cs				[For Behrens tests see I., pp. 276-279, and C.; see also Benedetti-Pichler and Bryant, Ind. Eng. Chem. [Anal.], 1938, 10, 107; Mikrochem, 1939, 26, 29.]
Cu	(a) $\alpha$ -Benzoin oxime ("cupron") and $\text{NH}_3$ vapour. (b) Dithio - oxamide (rubeanic acid) and $\text{NH}_3$ .	Green spot. Black spot.	0.5 $\mu\text{g.}/0.03 \text{ ml.}$ 0.03 $\mu\text{g.}/0.03 \text{ ml.}$	I.T.F.H.B.A. I.T.F.H.B.A.
F'	(a) Alizarin S, zirconium nitrate, and dil. HCl. (b) Zirconium <i>p</i> -dimethylaminoazophenylarsinate.	Yellow colour. Red spot.	0.6 $\mu\text{g.}/0.03 \text{ ml.}$ 0.15 $\mu\text{g.}/0.03 \text{ ml.}$	I.F.T.H.B.A. I.F.
$\text{Fe}^{\text{II}}$	(a) Dimethylglyoxime, tartrate, and aq. $\text{NH}_3$ .  (b) $\alpha\alpha'$ -Dipyridyl.	Red colour. Red colour.	0.03 $\mu\text{g.}/0.03 \text{ ml.}$ 0.5 $\mu\text{g.}/5 \text{ ml.}$	I.F.T.H. [See Wenger and Duckert, <i>Helv. Chim. Acta</i> , 1944, 27, 757, for a critical study of reagents for $\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}$ .] I.F.T.B. [See Cronheim and Wink, Ind. Eng. Chem. [Anal.], 1942, 14, 447, for use of <i>o</i> -nitrosophenol for $\text{Fe}^{\text{II}}$ .]
$\text{Fe}^{\text{III}}$	(a) KCNS.  (b) $\text{K}_4\text{Fe}(\text{CN})_6$ .	Red colour. Blue colour or precipitate.	0.15 $\mu\text{g.}/0.03 \text{ ml.}$ 0.1 $\mu\text{g.}/0.05 \text{ ml.}$	I.F.T.S. [See Peters and French, <i>ibid.</i> 1941, 13, 604.] I.F.T.C. Clarke and Hermance, <i>ibid.</i> 1937, 9, 292.

\* Value obtained by the writer.

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Ga	Morin.	Green fluorescence.	0.85 $\mu\text{g.}/5$ ml. [In ultra-violet light, 0.015 $\mu\text{g.}$ per 5 ml.]	I. [See Sandell, <i>ibid.</i> 1911, 13, 844, for a fluorescence reaction with 8-hydroxyquinoline; see Wenger and Duckert, <i>Helv. Chim. Acta</i> , 1942, 35, 699, for a critical study of reagents for $\text{Ga}^{+++}$ .]
Hg	(a) Diphenylcarb-azide. (b) Al.	Violet-blue colour. Activation.	0.1 $\mu\text{g.}/0.03$ ml. 0.001 $\mu\text{g.}/0.05$ ml.	I.F.T.H. I.F.T. [See Steigmann, <i>J.S.C.I.</i> 1942, 61, 51, for a test for $\text{Hg}^{++}$ using a photographic emulsion.]
I'	(a) Palladous chloride. (b) Bromine or potassium permanganate in alkaline solution, KI, acid, starch. (c) 2N-AcOH, 0.1N-NaNO <sub>2</sub> , and starch.	Brownish-black precipitate. Formation of iodate, and liberation of I <sub>2</sub> by acid KI. Blue colour. Blue colour.	1 $\mu\text{g.}/0.05$ ml. 0.1 $\mu\text{g.}/0.05$ ml. 1.0 $\mu\text{g.}/0.03$ ml.*	I.F.T. F.T. F.
K	(a) Sodium cobalt-nitrite (solid). (b) Sodium cobalt-nitrite (solid) + aq. AgNO <sub>3</sub> .	Yellow precipitate. Yellow precipitate.	2.4 $\mu\text{g.}/0.03$ ml. 0.6 $\mu\text{g.}/0.03$ ml.	I.F.T.C. I.F.T.
Li	KIO <sub>4</sub> , KOH, and FeCl <sub>3</sub> in 2N-KOH (+NaCl).	Yellowish-white precipitate.	0.24 $\mu\text{g.}/0.03$ ml.*	F. Proëke and Uzel, <i>Mikrochim. Acta</i> , 1938, 3, 105.
Mg	(a) <i>p</i> -Nitrobenzenazo-resorcinol ("magneson") and NaOH. (b) Titan Yellow.	Blue precipitate or colour. Red colour.	0.3 $\mu\text{g.}/0.03$ ml. 0.9 $\mu\text{g.}/0.03$ ml.	I.F.T.S.H.B.A. [See Newell <i>et al.</i> , <i>Z. anorg. Chem.</i> 1935, 225, 281; Mehlig and Johnson, <i>Ind. Eng. Chem. [Anal.]</i> , 1940, 12, 30.] I.F.T.H.B. [See Otto and Otto, <i>ibid.</i> 1941, 13, 65.]
Mn	(a) KIO <sub>4</sub> (+HNO <sub>3</sub> and H <sub>3</sub> PO <sub>4</sub> ). (b) KIO <sub>4</sub> and tetramethyldiaminodiphenylmethane (+AcOH).	Reddish-violet colour. Blue colour.	1 $\mu\text{g.}/0.03$ ml. 0.003 $\mu\text{g.}/5$ ml.	I.S.A. I.F.T. [See Wenger <i>et al.</i> , <i>Helv. Chim. Acta</i> , 1941, 24, 1143, for a critical study of reagents for $\text{Mn}^{++}$ .]

\* Value obtained by the writer.



Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Mo	(a) KCNS and Zn, or SnCl <sub>2</sub> , or Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	Red colour.	0.1 µg./0.05 ml.	I.F.T.A.
	(b) Potassium xanthate.	Reddish-violet colour.	0.04 µg./0.05 ml.	I.F. [See Rice and Yerkes, U.S. Bur. Mines, Rept. Invest. 3328, 1937, p. 37, for critical study of reactions for Mo.]
Na	(a) Magnesium uranyl acetate.	Yellow precipitate.	250 µg./5 ml.	I.C.T. [See Benedetti-Pichler <i>et al.</i> , Mikrochemie, 1939, 26, 29.]
	(b) Magnesium uranyl acetate+alcohol.	Yellow precipitate.	0.03 µg./5 ml.	I.C.T. [See also Caley and Rogers, Ind. Eng. Chem. [Anal.], 1943, 15, 32.]
Nb	Tannin (weakly acid oxalate solution + NH <sub>4</sub> Cl).	Red precipitate.	65 µg./5 ml.	I. W. R. Schoeller, "Analytical Chemistry of Tantalum and Niobium," London, 1937.
NH <sub>4</sub> <sup>+</sup>	(a) Sodium hydroxide.	Red litmus paper turned blue by gas evolved.	0.01 µg./0.05 ml.	I.F.T.
	(b) Potassium mercuric iodide ("Nessler's reagent").	Yellowish-red precipitate.	0.25 µg./5 ml.	I.T.
Ni	(a) Dimethylglyoxime (+ citrate and aq. NH <sub>3</sub> ).	Red precipitate or spot.	0.1 µg./0.03 ml.	I.F.T.H.B.C.
	(b) Dithio - oxamide (Rubeanic acid).	Purple precipitate or spot or ring.	2.5 µg./5 ml. or 0.005 µg./0.05 ml.	I.F.T.H.B. [For critical review of reagents for Ni <sup>++</sup> , see Wenger <i>et al.</i> , Helv. Chim. Acta, 1941, 24, 889.]
	(c) cycloHexane-1:2-dione dioxime.	Red precipitate or colour.	0.1 µg.	I. Wenger <i>et al.</i> , <i>l.c.</i>
NO <sub>2</sub> <sup>+</sup>	α-Naphthylamine and sulphanic acid.	Red colour.	0.006 µg./0.03 ml.	I.F.T.
NO <sub>3</sub> <sup>+</sup>	(a) Zn+α-naphthylamine and sulphanic acid.	Red colour.	0.05 µg./0.05 ml.	I.F.T.
	(b) Sodium hydroxide, and Al, Zn, or Devarda's alloy, litmus paper.	Ammonia evolved, and blue colour of litmus paper.	10 µg./0.05 ml.	F.T.
Pb	(a) Diphenylthiocarbazone ("Dithizone")	Red colour.	0.08 µg./0.1 ml.	I.F.T.S.H.B.
	(b) Copper acetate, KNO <sub>3</sub> , NaOAc, AcOH.	Black, cubic crystals.	0.2 µg./0.01 ml.	I.C.

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Pd	(a) Dimethylglyoxime. (b) Dimethylaminobenzylidenerhodanine. (c) See below, Pt metals.	Yellow precipitate. Red-violet precipitate or spot or ring.	0.0025 µg./0.03 ml.	I.F.C.T.H.B. I.F.
PO <sub>4</sub> <sup>'''</sup>	Ammonium molybdate and benzidine (+NaOAc)	Blue colour, spot or ring.	0.01 µg./0.03 ml.	I.F.T.A. [See West and Houtman, Ind. Eng. Chem. [Anal.], 1942, 14, 597, for interferences.]
Pt	Potassium iodide.	Red colour.	0.5 µg./0.03 ml.	I.T.
Pt metals.	Nickel acetate, and sodium hypophosphite.	Black precipitate of Ni due to accelerated reduction.		I.F. [See Fraser, Amer. Min. 1937, 22, 1016, for Behrens tests.]
Re	Stannous chloride and sodium tellurate (+HCl).	Black precipitate, due to catalysed reduction of TeO <sub>4</sub> <sup>'''</sup> .	0.01 µg./0.03 ml.	I. [See Wenger <i>et al.</i> , Helv. Chim. Acta, 1942, 25, 599, for critical study of the reactions of Re <sup>'''</sup> and ReO <sub>4</sub> <sup>'</sup> .]
Ru	(a) Dithio-oxamide (Rubeanic acid). (b) See Pt metals.	Blue colour.	0.2 µg./0.02 ml.	I.F.
S (as free sulphur).	Pyridine, and 2N-NaOH (or saturated aq. Na <sub>2</sub> CO <sub>3</sub> ).	Brown → green → blue colorations (or shades of blue).	2 µg./1 ml.	Sommer, Ind. Eng. Chem. [Anal.], 1940, 12, 368.
S', (S <sub>2</sub> O <sub>3</sub> <sup>''</sup> , CNS <sup>'</sup> , but not free S).	Sodium azide, iodine, and KI:	Nitrogen evolved (catalytic action).	0.005 µg./0.03 ml.	I.F.T.
Sb	Rhodamine-B (+HNO <sub>2</sub> ).	Violet colour or precipitate.	0.5 µg./5 ml.	I.T.F.B.A. [See Frederick, <i>ibid.</i> 1941, 13, 922, and Scott and Robins, <i>ibid.</i> 1942, 14, 206.]
Se	(a) Potassium iodide. (b) Thiourea.	Red-brown precipitate or spot. Red precipitate or colour.	1 µg./0.025 ml. —	I.F.T. I.T.
Sn <sup>II</sup>	(a) Dimethylglyoxime, ferric chloride, tartrate or citrate, aq. NH <sub>3</sub> . (b) Cacotheline.	Red colour. Red-violet colour.	0.05 µg./5 ml. 0.12 µg./0.03 ml.	I.T. I.F.S.H.B.A. [See Nowell <i>et al.</i> , <i>ibid.</i> 1935, 7, 26, for a critical study.]

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Sn (as metal)	(c) HCl and Zn.	Bunsen flame coloured blue.	0.03 $\mu$ g.	F. [See Kuznetsov, J. Appl. Chem. Russia, 1940, 13, 769, for a colour reaction for Sn <sup>IV</sup> .]
Sr	Sodium rhodizonate.	Brown spot, decolorised by dilute (1:20) HCl.	0.3 $\mu$ g./0.03 ml.	I.F.T.S.B.A.
Ta	Tannin (weakly acid oxalate solution + NH <sub>4</sub> Cl).	Yellow precipitate or colour.	200 $\mu$ g./5 ml.	I. W. R. Schoeller, "Analytical Chemistry, of Tantalum and Niobium," London, 1937.
Te	Thiourea.	Yellow precipitate or colour $\rightarrow$ black with ether + aq. NH <sub>3</sub> .	0.05 $\mu$ g./5 ml.	I. -
Th	(a) 8-Hydroxyquinoline in EtOH or COMe <sub>2</sub> . (b) H <sub>2</sub> O <sub>2</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , BaCl <sub>2</sub> , 0.1N-AcOH.	Yellow-orange red precipitate. White precipitate.	3 $\mu$ g./0.5 ml. 0.5 $\mu$ g./4 ml.	I. Wenger and Duckert, Helv. Chim. Acta, 1942, 25, 1110. Wenger and Duckert, <i>ibid.</i> 1942, 25, 1110.
Ti	(a) H <sub>2</sub> O <sub>2</sub> and dil. H <sub>2</sub> SO <sub>4</sub> . (b) Dihydroxymaleic acid. (c) Chromotropic acid.	Yellow-orange colour. Red-brown colour. Violet colour.	1.2 $\mu$ g./0.03 ml. 1 $\mu$ g./5 ml. 0.1 $\mu$ g./0.05 ml.	I.F.T.A. I. I.F.B.A.
T	(a) Potassium iodide. (b) Phosphomolybdic acid and HBr.	Yellow precipitate. Blue colour.	0.6 $\mu$ g./0.05 ml. 0.19 $\mu$ g./0.03 ml.	I.F.T.C. I.F.
UO <sub>2</sub> <sup>++</sup>	K <sub>4</sub> Fe(CN) <sub>6</sub> .	Brown precipitate or colour.	0.55 $\mu$ g./0.03 ml.	I.F.T. [See Wenger <i>et al.</i> , <i>ibid.</i> 1945, 28, 291, for critical study of the reactions of UO <sub>2</sub> <sup>++</sup> .]
V	(a) Hydrogen peroxide (+ HNO <sub>3</sub> ). (b) Dimethylglyoxime, ferric chloride, and aq. NH <sub>3</sub> .	Red-brown colour. Red colour.	1.5 $\mu$ g./0.03 ml. 0.6 $\mu$ g./0.03 ml.	I.F.T.A. I.F.T.
W	Stannous chloride and HCl	Blue precipitate or colour.	3 $\mu$ g./0.03 ml.	I.F.T.

Element or ion.	Reagent.	Reaction.	Limit of identification.	References.
Zn	(a) Ammonium mercuric thiocyanate, copper sulphate (extract with amyl acetate).	Violet precipitate.	3 µg./0.03 ml.	I.S.C.
	(b) "Dithizone" in $\text{CCl}_4$ .	Red coloration.	0.03 µg./0.03 ml.	I.F.T.H. [See Wenger and Duckert, <i>ibid.</i> 1942, 25, 406, for a study of reagents for $\text{Zn}^{++}$ .]
Zr	(a) 4-Dimethylamino-azobenzene - 4' - arsinic acid (+HCl).	Brown spot.	0.06 µg./0.03 ml.	I.F.B.A.
	(b) Alizarin (+dil. HCl).	Red-violet precipitate or colour.	0.3 µg./0.03 ml.	I.F.H.

## KEY TO REFERENCES.

- I. "Tables of Reagents for Inorganic Analysis." First Report of the International Committee on new analytical reactions and reagents. Leipzig, 1938.  
[Deals with new reagents discovered from the end of 1910 to the end of 1936, and some of the older reagents. References are as complete as possible to the end of 1936. Data given include method of executing a test, reaction observed, limit of identification and limiting concentration, and interferences by other components. A special feature is the recommendation of the most suitable and trustworthy tests.]
- F. F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 3rd ed., Leipzig, 1938. [Translations: Theoretical Part, "Specific and Special Reactions for Use in Qualitative Analysis," New York, 1940; Practical Part, "Spot Tests," New York, 1939; "Laboratory Manual of Spot Tests," New York, 1943.]
- T. F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. I, Qualitative Analysis, New York, 1937.
- G. E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," New York, 1938.
- S. N. Strafford, "Detection and Determination of Small amounts of Inorganic Substances by Colorimetric Methods," Royal Institute of Chemistry, London, 1933.
- H. Hopkin and Williams, Ltd., "Organic Reagents for Metals and for certain Acid Radicals," London, 1943.
- B. British Drug Houses, Ltd., "B.D.H. Book of Organic Reagents for Analytical Use," London, 1941.
- A. Articles on DROP REACTIONS ("SPOT" TESTS) and COLORIMETRY, Vol. II, 570r and 669b, respectively.

References to the literature are well covered by the above-mentioned works. Additional references have been added to the table. Some of the articles on Analytical Chemistry in the Annual Reports of the Chemical Society, London, review recent work on the subject. J. Mellan, "Organic Reagents in Inorganic Analysis," Philadelphia, 1941, contains much information relating to drop reactions, with numerous references to the literature concerning each reagent. A brief review of the subject is given by Feigl, "Organic Reagents in Organic Analysis," Ind. Eng. Chem. [Anal.], 1936, 8, 401. Drop reactions of special interest theoretically are described and discussed in three recent articles by Feigl, J. Chem. Educ. 1943, 20, 137, 171, 240, 298; 1944, 21, 294, 317, 479; 1945, 22, 36, 342.

The table above contains no reference to the interferences to which a test is subject. Many of these will be found mentioned in the works referred to, and particularly in the special references given in the last column of the table. Any attempt at tabulating interferences to single tests would have been only misleading, and hence has been omitted. It must be remembered, however, that these interferences are often numerous, and whenever uncertainty exists the wisest course of action is to check the validity of a test at the time it is made by means of a control or blank experiment performed under conditions as nearly as possible identical with those under which the test itself is carried out.

## APPLICATIONS TO PRACTICAL PROBLEMS.

A glance at Feigl's book on "Tüpfelreaktionen" will show how many and varied are the uses to which drop reactions can be put in the investigation of technical problems, and how wide is the field that these problems cover. Only a brief review of some of these applications can be attempted here, but this will serve to give an idea of their scope and interest.

**Qualitative and Quantitative Inorganic Analyses on a Macro-scale.**—In ordinary macro-analyses drop reactions provide admirable confirmatory tests after the main separations into groups and sub-groups have been effected. The cinchonine-potassium iodide test for bis-

mut, the Rhodamine-B test for antimony, the "cation" test for cadmium, and the "magneson" test for magnesium, to mention a few, are good examples of this. Drop reactions can also be made to deal very successfully with the small precipitates, due possibly to faulty methods of separation, that so often are troublesome in an ordinary analysis. They have been used, too, for identifying the "insolubles" of chemical analysis (see Feigl, Mikrochem. 1936, 20, 198; and, F., p. 365), for detecting acidity and basicity in slightly soluble materials (Feigl *et al.*, Ind. Eng. Chem. [Anal.], 1942, 14, 316, 519), and for testing the purity of chemical reagents. In quantitative work they serve in examining filtrates for completeness of precipitation, and

for the contamination of precipitates by co-precipitated ions.

**Qualitative Inorganic Analysis on Micro- and Semi-micro-scales.**—Several schemes for the systematic analysis of small amounts of material on the micro-scale have been known for some time (*see* F., p. 350; T., Vol. I, p. 493; and C. J. Engelder, T. H. Dunkelberger, and W. J. Schiller, "Semi-micro Qualitative Analysis," New York, 1936), and the more recent work includes a series of investigations for the separation of cations into groups, their identification, and estimation on a milligram-scale (Benedetti-Pichler and co-workers, *Mikrochem.* 1936, 19, 239; *Mikrochem.*, Molisch *Festschr.* 1936, 3, 36; *Ind. Eng. Chem. [Anal.]*, 1937, 9, 589; 1938, 10, 107; 1939, 11, 117, 294; *Mikrochem.* 1938, 24, 16), the separations being based mainly on those of A. A. Noyes and W. C. Bray ("A System of Qualitative Analysis for the Rare Elements," New York, 1927). By means of a special technique (Benedetti-Pichler *et al.*, *Ind. Eng. Chem. [Anal.]*, 1937, 9, 483; 1942, 14, 813; 1943, 15, 227) separations for the qualitative analysis of 1  $\mu$ g. of solid material are being investigated.

The various Noyes-Bray groups are also being put on a semi-micro-scale (Miller and Lowe, *J.C.S.* 1940, 1258, 1263; Miller, *ibid.* 1941, 72, 786; 1943, 72). In all these schemes, drop reactions play an essential part. (*See also* Dobbins *et al.*, *J. Chem. Educ.* 1939, 16, 94; Dobbins and Southern, *ibid.* 1942, 19, 479, for other, less complicated, separations.)

**Mineralogy and Petrology.**—The mineralogist, and the geochemist are often faced with the problem of identifying small quantities, sometimes only tiny particles, of opaque materials for which microscopical examination gives little or no help. Here the discriminating use of drop reactions often serves to identify the constituents of the rock or mineral, and even when valuable information has been obtained by petrological examination, drop reactions can frequently provide a quick and easy means of establishing the presence of certain elements in many types of rock, ore, and mineral (*see* Feigl, *l.c.*; Watson, *Min. Mag.* 1935, 24, 21). The Behrens tests are popular with some mineralogists, particularly American (*see* M. N. Short, "Microscopic Determination of Ore Materials," U.S. Geol. Survey, Bulletin 914, 1940), and a selection of tests suitable for determinative mineralogy has been made (Staples, *Amer. Min.* 1936, 21, 613).

Recent developments in the contact-print method for the determination and localisation of metallic minerals (Gutzeit, *Amer. Inst. Min. Met. Eng. Publ.*, 1942, No. 1457) are of interest. In this method, gelatin-coated paper is impregnated with a suitable attacking reagent, pressed on the polished surface of the mineral specimen, and then removed for development in a reagent that is selective for the desired constituent. The elements in a polished surface can thus be identified and located by colour reactions with little or no damage to the specimen. The method is reminiscent of that used for the location of phosphate in a rock by means of ammonium molybdate and benzidine (Feigl,

*l.c.*), and for the identification of mineral particles that cannot be recognised by microscopical examination (Rey and Zeicher, *Bull. Soc. chim. Belg.* 1937, 46, 173; *see also* Yagoda, "Analytical patterns in the study of mineral and biological materials," *Ind. Eng. Chem. [Anal.]*, 1943, 15, 135; and Yagoda, "Localisation of copper and silver sulphide minerals in polished sections by the potassium cyanide etch pattern," *Amer. Min.* 1945, 30, 51).

**Metallurgy.**—Of the many applications of these drop reactions to metallurgy, which range from reactions on the surface of the metal (*see*, for example, Evans *et al.*, *Analyst*, 1945, 70, 75) to complete dissolution and systematic analysis of the sample or the search for one particular constituent or impurity, one example will be given, as it typifies the combination of electrochemical technique with colour reactions. In this "electrographic" method, the metal or alloy is made the anode, and graphite or a suitable metal the cathode, whilst filter-paper moistened with an electrolyte and the reagent giving the colour reaction completes the circuit between the electrodes. On passing a small current for a few seconds or less, the metal dissolves anodically and reacts with the reagent in the paper to give the identifying colour. In this way, chromium has been recently detected in stainless steels, in alloys, and in plating by the hydrogen-peroxide test (Calamari, *Ind. Eng. Chem. [Anal.]*, 1941, 13, 19), and molybdenum in steel alloys by the thiocyanate-stannous chloride reaction after precipitation as lead molybdate (*idem et al.*, *ibid.* 1943, 15, 71; *see also* F., p. 481, and Hunter, Churchill, and Mears, *Metal Progress*, 1942, 42, 1070; the electrographic method has also been applied to minerals). The method is very quick to carry out, and does little or no damage to the specimen. (*See also* Niessner, *Angew. Chem.* 1939, 52, 721; Lerner, *Ind. Eng. Chem. [Anal.]*, 1943, 15, 416, for detecting gold in plating).

**Other Applications.**—As examples of recent applications showing the steady extension of these reactions in many fields, mention can be made of the identification of drugs (Rojahn *et al.*, *Pharm. Zentr.* 1937, 78, 81, 127, 146), the detection of traces of nickel carbonyl in oils and gases by its reactions with dimethylglyoxime and dithizone (Steiger, *Mikrochem.* 1937, 22, 216), the distribution of injected heavy metals in cell tissues and in the cell contents of plants (Prát, *Mikrochem.*, Molisch *Festschr.* 1936, 342), or that of chlorides on the surface of wood or contaminated fabric (Lennox, *J. Proc. Austral. Chem. Inst.* 1936, 3, 313), the recognition of pigments from paintings without damage to the latter (Augusti, *Mikrochim. Acta*, 1938, 3, 239), and the detection of the solubility corrosion of metals by sea-water (Atkins, *Trans. Faraday Soc.* 1937, 33, 431). In criminology, too, there is clearly a large field of application.

Finally, wide and growing use is now being made of these reactions in the qualitative analysis of organic substances (Feigl, *l.c.*).

**Conclusion.**—The study of drop reactions with their utilisation of organic compounds involves much that is of theoretical interest on subjects such as co-ordination compounds, the

sensitivity of chemical reactions, their masking by different reagents, and their enhancement by the catalytic action of certain substances, the activity of certain atomic groupings towards different ions, and the effect that capillary phenomena have in chemical processes, whilst on the practical side these reactions provide a valuable analytical weapon for attacking with relative ease problems that could be solved by the older methods often only with difficulty and much uncertainty.

L. S. T.

### MICROCHEMICAL OPERATIONS.

**Sublimation.**—Sublimation is useful in the purification, separation, and identification of organic compounds. Under suitable conditions many organic compounds, including glucosides and amino-acids, sublime to give characteristic sublimate, which may frequently be used to identify a substance that decomposes below its melting-point. A minute crystalline sublimate may be used for micro-melting-point determinations.

The best crystalline sublimate is obtained when its formation is slow, and the cooling distance is small, the temperature of the receiver being only a few degrees lower than that of sublimation.

In Soltz's apparatus (Fig. 1), the sublimation is carried out in a stream of air, and the sublimate is filtered from blown particles by passing through a wall of coarsely fritted glass, and received on a condenser through which water is circulating. The sample may be placed in a small boat in the right half of the tube, or on the glass walls of the apparatus, which is heated in a metal block; the temperature of sublimation is read on a thermometer inserted in the block. This apparatus may be used under either ordinary or reduced pressure, and is useful

for preparing large samples of sublimate (5-15 mg.) for subsequent quantitative analysis.

Eder's apparatus (Fig. 2) is adapted for the sublimation of very small amounts of material for microscopic examination and for melting-point determinations under the microscope (Eder and Haas, *Microchem.*, *Enrich Festschrift*, 1930, 43). The sample (0.1 mg. is sufficient) is placed in the bulb in the bottom of the tube and heated in a suitable bath; the sublimate is formed on the underside of the cover-slip, which should be only a few mm. above the surface of the heating bath, in order to ensure good crystal formation. It is obvious that the heating must be carried out very cautiously and slowly, or the sublimate will disappear, as the cooling range is only a few degrees. With this apparatus very low pressures may be used, and it is especially suited for use with substances of which sublimation is difficult, e.g., hydroxyproline. There is no definite "sublimation temperature," and the required temperature can only be defined em-

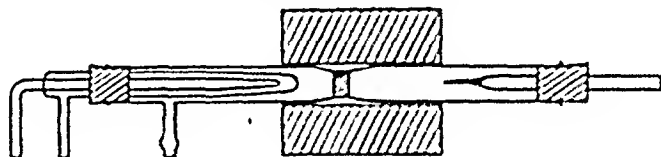


Fig. 1.

pirically according to the apparatus and the conditions.

Sublimation may also be carried out under the microscope, any type of melting-point block designed for the microscope stage being used. It is not generally satisfactory to use reduced pressure, but the extremely short cooling distance (about 0.5-3 mm.) aids the formation of good crystalline sublimate. When the melting-point block (Fig. 3) is used, the receiver is often placed on the top surface of the block, but two cover-slips separated by thin strips of glass may

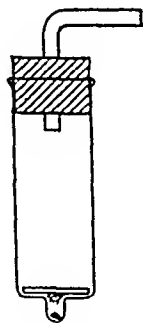


Fig. 2.

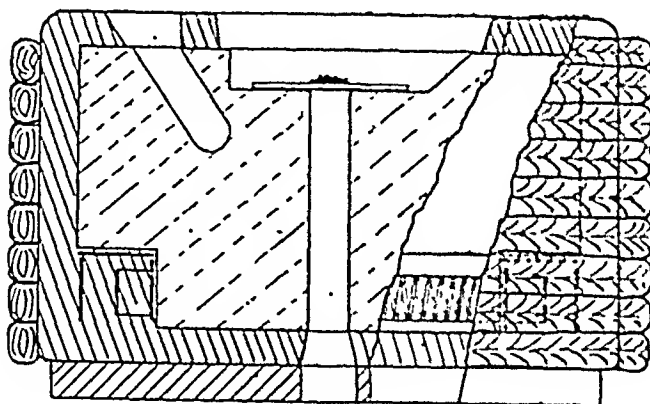


Fig. 3.

be used, one above the other, for material and sublimate. Only very small samples should be used in this apparatus; about 30-50  $\mu$ g. of impure material is ample, or a few small crystals of fairly pure material.

**Determination of Melting-Point.**—The method of melting-point determination under

the microscope offers the advantages that all the accompanying phenomena are observed, and even substances which decompose before melting may be identified by the appearance or melting-point of their decomposition products.

There are a large number of different designs for heating blocks suitable for the microscope

stage. Electrical heating is the most effective and an accurate thermometer is preferable to a thermoelectric couple for reading the temperature. Blocks may be constructed for use with either reflected or transmitted light; the latter has the advantage that polarised light may be used, in which case anisotropic substances disappear from view at their melting-point, owing to the formation of an isotropic liquid. As a very large number of substances are doubly refracting, this type of block renders the reading of the melting-point very simple.

A block may be constructed in any efficient workshop. Fig. 3 shows a home-made block (H. V. A. Briscoe and J. W. Matthews, "Microchemical Methods suitable for General Analytical Practice," Royal Institute of Chemistry Lecture, 1934) for use with transmitted light. A good thermometer, preferably very short, to obviate stem correction, is inserted in the hole in the top, a drop of mercury ensuring perfect contact.

Fuchs (Mikrochim Acta, 1937, 2, 317) describes a heating-block of polished copper, for use with reflected light, which has a circular built-in thermometer and has the advantage that the melting of the sample and the thermometer may be observed simultaneously, one eye being used for each. The crystals to be observed are placed on a small polished black plate on the block.

In all types of electrically heated blocks the speed of heating is regulated by an external resistance. At first the rate may be 10–20°C. per minute, until 10–15°C. below the melting-point, when the rate is reduced to 2°C. per minute. Very volatile substances should be heated rather more rapidly in the region of their melting-point, to avoid sublimation. The crystals under examination are heated between two extremely thin cover-slips. Melting-points below 200°C. may be read with an error not exceeding  $\pm 1^\circ$  ( $\pm 2^\circ$  above 200°C.).

A simple and accurate design for a melting-point apparatus consists of a thermometer with a flat-sided bulb on which are placed the crystals under observation; this fits in a metal block which is heated either electrically or by means of a small burner.

**Determination of Boiling-Point.**—Boiling-point determinations may be carried out by Emich's method (F. Emich, "Microchemical Laboratory Manual," trans. by F. Schneider, Chapman and Hall, 1932) with very simple apparatus (Fig. 4); a capillary tube of about 1 mm. bore is drawn out to a hair-fine capillary at one end (Fig. 5). The liquid under examination runs up the capillary tube when the hair-fine tip is inserted into it, filling it to a length of about 1–2 cm. The tip is then rapidly sealed in such a way that a small bubble of air is enclosed below the liquid. One or more of such tubes are then fixed, with a drop of liquid, on a microscope slide which is attached by a rubber band to a thermometer and immersed in the heating bath. On heating, the bubble expands slowly until the boiling-point is reached, when it suddenly increases in volume, driving the drop of liquid to the level of the surface of the bath.

**Extraction.**—A number of different types of micro-extraction apparatus have been devised,

usually with some particular problem in view, or for use with the type of microbalance available. Gorbach's apparatus for the extraction of fat was specially made for use with the torsion microbalance of small load capacity. As this balance is a rarity, the Titus and Melocke extractor, for use with an ordinary

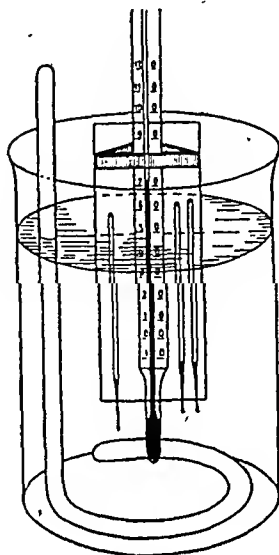


FIG. 4.



FIG. 5.

microbalance of the type used by Pregl, is of more general application (Ind. Eng. Chem. [Anal.], 1933, 5, 286). It is a micro-Soxhlet extractor, designed originally for the determination of the ether extract of lake-water residues prepared by the evaporation of known volumes of water. Its efficiency as a fat extractor, as tested by comparison with the Soxhlet macro-extractor, is shown in the Table below.

Sample.	Macro, %.	Micro, %.
Dry skim milk . . .	0.08 0.08	0.07 0.09
Casein . . . . .	0.16 0.15	0.16 0.19
Feed sample . . .	5.0 —	5.43 5.43

Typical results obtained in the extraction of lake-water residues are given below.

Sample.	Weight of sample, mg.	Weight of extract, mg.	%.
I	15.671 12.785	0.164 0.138	1.05 1.08
II	14.903 13.800	0.219 0.205	1.47 1.49
III	10.603 13.605	0.037 0.050	0.35 0.37

tion, and if the tip is placed only about 1 mm. above the precipitate, it can remove almost all the liquid.

**Crystallisation.**—Crystallisation may be carried out on almost any type of small apparatus, such as a microscope slide heated on a micro-melting-point block, a micro-centrifuge tube, heated in a metal block or over the water bath, a micro-beaker of capacity 3–10 ml., or a micro-Kjeldahl tube. The micro-Kjeldahl tube (20 ml. capacity) is very convenient for working with very volatile solvents, and may be fitted with a long glass tube as reflux condenser and heated in warm or hot water. When the reflux tube is removed, as much of the solvent as is desirable may be evaporated, and the last ml. quantitatively transferred to another vessel, about three washings of 1 ml. being used, as in the normal micro-Kjeldahl procedure. The use of micro-Kjeldahl tubes has proved valuable in a number of biological preparations where the amount of starting material is, of necessity, large in relation to the quantity of product.

Where economy of material is of primary importance, it is advisable to use sealed capillary tubes for recrystallisation. Capillary tubes of 1–2 mm. diameter and 7–8 cm. long are a convenient size. A constriction is melted about 2–3 cm. from one end to hold a small plug of asbestos in place. Both ends of the capillary are then drawn out and the solution drawn in at the longer end. The opposite end is sealed first, and, after this has cooled, the other end. The tube is cooled to the desired temperature in a freezing mixture and then centrifuged so that the liquid is filtered through the asbestos. The capillary is then cut between the crystals and mother liquor, each of which can be further dealt with as necessary.

**Distillation.**—Micro-distillation is a simple operation, and the apparatus is varied according to the temperature and the number of fractions desired. Smith's apparatus (Fig. 8) is all glass,

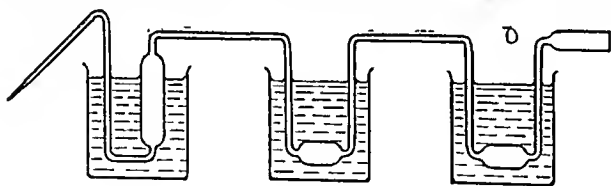


FIG. 8.

drawn out of glass tubing of 5–10 mm. diameter; the original tubing is left as a series of bulbs, and the drawn-out portions are bent round so that each bulb will fit in a bath heated at the desired temperature. Ordinary or reduced pressure may be used. The bulbs are severed from each other when the distillation is complete.

Another distillation apparatus is shown in Fig. 9; the small thermometer hangs on a hook under the ground-in stopper, which also carries a capillary inlet. Micro-distillation can be carried out with micro-Kjeldahl tubes as distilling flasks.

Simple distillations of a very small amount of volatile liquid from a relatively large bulk, may be carried out in Pichler's apparatus (Fig. 10);

this consists of a small pear-shaped flask with a long narrow neck in which a bulb is blown, and

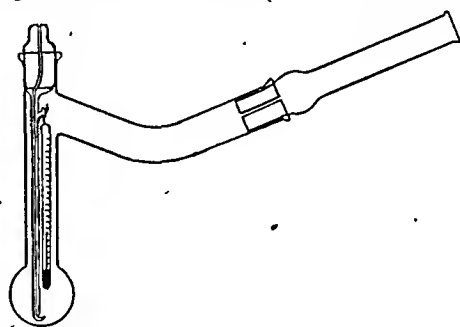


FIG. 9.

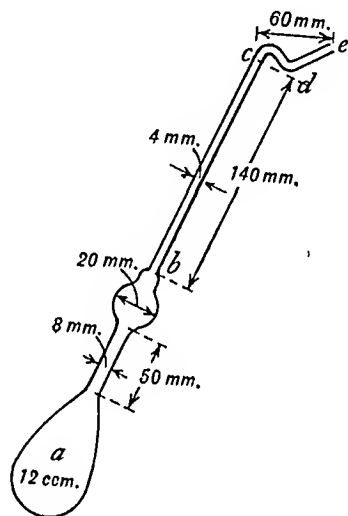


FIG. 10.

the top of the neck bent as shown in the figure. The volatile distillate condenses in the bend at the top of the neck and can be removed by means of a capillary tube drawn out to a hair-fine tip.

**Fluorescence.**—A large number of substances exhibit the phenomenon of fluorescence in ultra-violet light, and such substances can readily be detected under the microscope, light from a carbon arc, or other similar source, being focussed by a lens system on to the platform of the microscope. The use of the fluorescence microscope is especially important in the examination of food and drugs, and pharmaceutical products, for a substance with a typical fluorescence is easily distinguished under the microscope, even in the presence of excess of foreign material.

J. W. M.

## ORGANIC MICRO-ANALYSIS.

### DETERMINATION OF MOLECULAR WEIGHT BY THE METHOD OF A. RIECHE.

Rieche's apparatus (Ber. 1926, 59 [B], 218) (Fig. 1) is more suitable for solvents of higher



boiling-point, such as benzene, water, pyridine, or glacial acetic acid, although it entails the use of 4 ml. of solvent and, consequently, of 15–25 mg. of the substance. Even a transitory overheating of the Beckmann thermometer is almost excluded in this method, as it is always surrounded by a mixture of the boiling liquid and of its vapours. The liquid, which is boiled in the flask, *K*, is continually projected, together with its vapour, on to the thermometer through

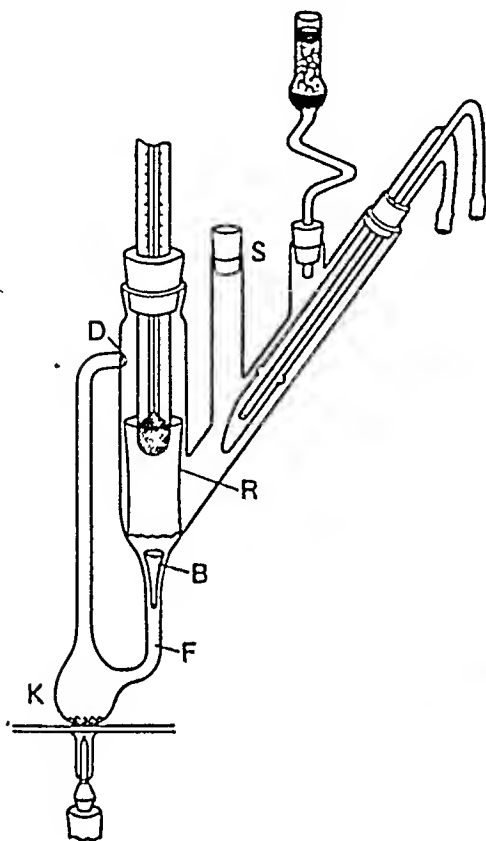


FIG. 1.

the nozzle, *D*; the vapour condenses in the condenser, whilst the liquid falls back into the boiling-flask through the tube, *F*. The tube is provided with a small baffle-cone, *B*, which prevents the liquid from passing in the reverse direction. The liquid is heated over an asbestos-covered wire gauze by means of a micro-burner. Superheating is avoided by the use of platinum tetrahedra weighing 0.3 g., and the apparatus is protected against air currents by a simple cardboard cylinder. As in this apparatus a certain proportion of the substance is always present in the vapour form, the results are usually slightly low, but never by more than 5%.

In order to carry out a determination, the platinum tetrahedra are inserted in the cleaned and dried apparatus, after which the baffle-cone is introduced and the thermometer also inserted by means of a tight-fitting cork, and carefully adjusted so that the bulb is completely covered by the inner tubular cylinder, *x*, in which position its lowest point is about 5 cm. below the upper rim of the apparatus. The whole assemblage is then clamped into a stand above the

asbestos-covered wire gauze and surrounded by a vertical cardboard cylinder. By means of a tared pipette, 4 ml. of solvent are added through the side-tube, *s*, which is then closed with a cork. The second side-tube is then closed with a calcium-chloride tube, and the condenser, which is completely dry, is so inserted that it does not touch the wall of the tube at any point. The micro-burner is placed exactly under the centre of the boiling-flask at a distance of 1–3 cm. below the gauze, so that the luminous point of the flame just touches the latter. If the heating is too strong it will be found that the liquid merely boils in the descending tube and that the nozzle does not act; under these conditions the thermometer reading is not constant. This difficulty is overcome by reducing the flame and raising it to a shorter distance from the gauze.

When the temperature has remained constant to within 0.002 c. throughout 5 minutes, the first tablet, weighing 15–25 mg., is introduced through the side-tube, *s*. It is sufficient to weigh this to within 0.1 mg. After 2 or 3 minutes the second temperature reading is taken. If this remains constant throughout a further 2 minutes, a second tablet is added, and the third reading of the temperature is taken after remaining constant for another 2–3 minutes.

If, when using pyridine or glacial acetic acid, it is found that the thermometer bulb is sprayed with a foaming liquid which spurts into the descending tube, the thermometer should be raised to such a position that its bulb is situated only 1–2 cm. below the nozzle.

For substances and solvents which are liable to be superheated, Rieche (*Chem.-Ztg.* 1928, 52, 923) recommends boiling the solvent in a paraffin bath.

#### DETERMINATION OF HALOGENS, SULPHUR, AND ARSENIC BY THE BOMB METHOD.

[See Beamish, *Ind. Eng. Chem. [Anal.]*, 1933, 5, 348; Elek and Hill, *J. Amer. Chem. Soc.* 1933, 55, 2550 (halogens); *idem, ibid.*, p. 3479 (sulphur); Parr, *ibid.* 1908, 30, 764 (use of sodium peroxide); Beamish and Collins, *Ind. Eng. Chem. [Anal.]*, 1934, 6, 379 (arsenic); J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Elementary Analysis," J. Wiley and Sons, Inc., 1938, p. 125.]

#### Determination of Halogens.

**Principle.**—The organic halogen compound is fused with a mixture of potassium nitrate sodium peroxide and cane sugar in a micro bomb, to yield ionisable halogen which is precipitated and weighed as silver halide.

**Apparatus.**—The bomb (Fig. 2) for the fusion consists of a fusion cup of 25 mm. depth and 13 mm. inside diameter, and is made of "illium" (an alloy containing Ni 58.40, Cr 28.80, Cu 7.95, Mo 3.52, W 2.38, Mn 1.72, Si 0.70, Fe 3.10, C 0.32%) or nickel. Its wall is 1.5 mm. thick and has a lip 3 mm. wide, on which the lid, which serves as a cover, rests. The cup has a rounded base and a small eyelet at the bottom. The lid of the bomb is held securely in position by an arched clamp with a tight-fitting screw.

*Reagents.*—All reagents must be halogen-free.

Potassium nitrate.  
Sodium peroxide.  
Concentrated nitric acid.  
Dilute nitric acid (0.1%).  
Silver nitrate solution (5%).  
Hydrazine sulphate.  
Cane sugar.

*Procedure.*—Three hundred milligrams of a mixture of potassium nitrate and cane sugar in the proportion of 3:1 should be placed on the bottom of the bomb and about 5 mg. of the sample on the surface of the mixture. To this mixture is added 1.5 g. of sodium peroxide; the lid is then screwed tight and the contents are

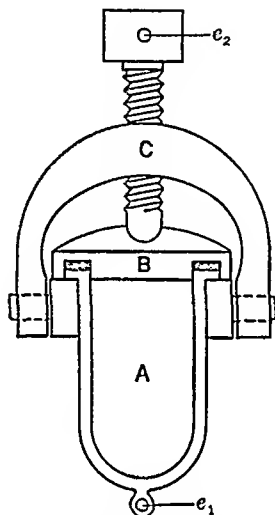


FIG. 2.—BOMB.

A, Cup; B, Lid; C, Screw-clamp;  $e_1$  and  $e_2$ , Eyelets

thoroughly mixed by shaking the bomb. It is important to mix thoroughly to bring about complete oxidation. After tapping the bomb repeatedly so that the contents settle to the bottom, it is ready for the fusion.

The bomb is held by the milled head of the clamp screw, either with tongs or by a piece of stout wire passed through the eyelet in the head of the screw, and gradually introduced into the upper part of a Bunsen flame. The fusion is complete in about 10 seconds; the exact time can be determined readily because the disturbance within the bomb can be felt. It is advisable to hold the bomb in the flame for an additional 15 seconds in order to fuse the entire reaction mixture. A few seconds afterwards the bomb is cooled under the tap.

The bomb is first rinsed on the outside with distilled water, and then opened, and the inside of the lid is washed with hot distilled water. The washings are collected in a Pyrex test tube. The cup is placed in the test tube and enough hot distilled water, about 15 ml., is added to cover the bomb. The test tube is shaken to ensure complete solution of the fusion mixture. After the fusion mixture has completely dissolved, the cup is removed with a looped nickel

wire and rinsed with distilled water, and the liquid added to the original solution, which is cooled in an ice bath and acidified with 5 ml. of concentrated nitric acid. The solution is filtered, with slight suction, into another test tube, and the filtrate heated with 1 ml. of 5% silver nitrate solution. Chlorides or bromides are usually precipitated immediately, but with iodides, a precipitate may not be formed; this is due to the fact that the iodide is oxidised to iodate.

This oxidation does not occur with chlorides and only to a slight extent with bromides, but it is practically quantitative with iodides. Whether a precipitate appears or not, the solution is placed on a steam bath and 100 mg. of finely powdered hydrazine sulphate added. The test tube should be left on the steam bath until the precipitate has coagulated; then the solution is cooled, and the resulting precipitate filtered on to a filter tube, washed with 60 ml. of 0.1% nitric acid solution, dried, and weighed. A complete analysis requires about 45 minutes, and two analyses can be made in an hour when two bomb cups are used.

It is usual to weigh out the required quantities of sodium peroxide, potassium nitrate-sugar mixture, and hydrazine sulphate into small test tubes, and to mark the level of the reagent in the test tube. Since the amount of reagent used needs to be only approximate, later quantities can be measured instead of being weighed.

#### Determination of Sulphur.

*Principle.*—The organic compound containing sulphur is fused with a mixture of potassium nitrate, sodium peroxide, and cane sugar in the metal bomb. The presence of the oxidising agents ensures quantitative oxidation of the sulphur to alkali sulphates. The sulphate thus formed is precipitated with barium chloride, and the resulting barium sulphate precipitate weighed.

*Apparatus and Reagents.*—The apparatus and the reagents, except the 10% barium chloride solution, are the same as in the halogen determination. It is important, however, that the rubber washer of a new bomb is boiled with caustic soda before being used. The reagents must be free from sulphur or its oxidation products.

*Barium chloride solution (10%):* Ten grams of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  of analytical purity) are dissolved in 100 ml. of distilled water.

*Procedure.*—In the cup of the bomb is placed 0.3 g. of a mixture of potassium nitrate and cane sugar (3:1), and 4–8 mg. of the substance to be analysed are added. The sample is covered with 1.5 g. of sodium peroxide, and after clamping the lid in position the bomb is well shaken to effect thorough mixing. Fusion and subsequent dissolving of the fusion mixture are carried out as described for the halogen determination. The resulting solution is cooled in an ice-bath, and then 5 ml. of concentrated hydrochloric acid are slowly added. The acid solution is filtered on a small Buchner funnel to

remove particles of carbon, and both test tube and filter are rinsed with distilled water.

The filtrate is transferred in 10- to 20-ml. portions to a well-steamed 50 ml. round-bottom Pyrex glass dish with a spout; 0.5 ml. of 10% barium chloride solution are added to the liquid in the dish and the whole evaporated to dryness. The solid residue is moistened with 10% hydrochloric acid solution, and the evaporation repeated. The final solid residue is taken up in 20-30 ml. of distilled water, and allowed to stand for 12 hours. The precipitate is then collected, dried, and weighed.

#### Determination of Arsenic.

*Principle.*—The organic arsenic compound is fused in the bomb with sodium peroxide, in the presence of sucrose, to give arsenic acid, which is determined iodometrically.

*Procedure.*—A quantity of sucrose, 20-25 mg., is placed in the bomb, and the weighed sample added. The amount of substance taken for analysis is adjusted to contain 1.5-3 mg. of arsenic. Approximately 1 g. of sodium peroxide is added to the material in the bomb; the bomb is tightly screwed and shaken well to effect thorough mixing of the substance with the reagents. The bomb is tapped repeatedly to ensure settling of the charge on the bottom of the cup, and then ignited by heating it in the tip of a small hot flame for about 40 seconds. The bomb should be cooled before being plunged in cold water, and when it has cooled sufficiently to permit its handling, the lid is removed and rinsed with distilled water, which is collected in a Pyrex test tube. The cup is placed in the

test tube and enough distilled water added to cover it, and then the contents of the test tube are heated over a small flame to dissolve the melt. When the fusion mixture has completely dissolved, the cup is removed with a looped nickel wire and rinsed thoroughly with distilled water. The test tube is then placed on a steam bath and the liquid concentrated to a volume of about 10 ml.; the heating also removes hydrogen peroxide. Then the solution is cooled, 12 ml. of concentrated hydrochloric acid are added, and the liquid is allowed to come to room temperature by placing the test tube in a water bath. One ml. of freshly prepared 10% potassium iodide solution is added, and the liquid is allowed to stand for exactly 3 minutes and titrated with 0.01N. sodium thiosulphate solution until only a faint yellow colour remains. Upon addition of 3 drops of 1% starch indicator solution, the titration is completed to the usual end-point, which is reached when the liquid remains colourless for at least 5 minutes. A blank titration of the reagents should be carried out, and the blank value, which should not amount to more than 0.3 ml., must be deducted.

#### DETERMINATION OF CARBON AND HYDROGEN.

After considerable experience with the original Pregl carbon and hydrogen apparatus it has been found that the chief sources of error are attributable to the use of rubber connections, and their elimination as far as possible is an important factor in ensuring accurate results. The modified apparatus (due to W. F. Boston) (Fig. 3) consists of two electric preheaters, A, 4 in. long, with a filling of platinised asbestos

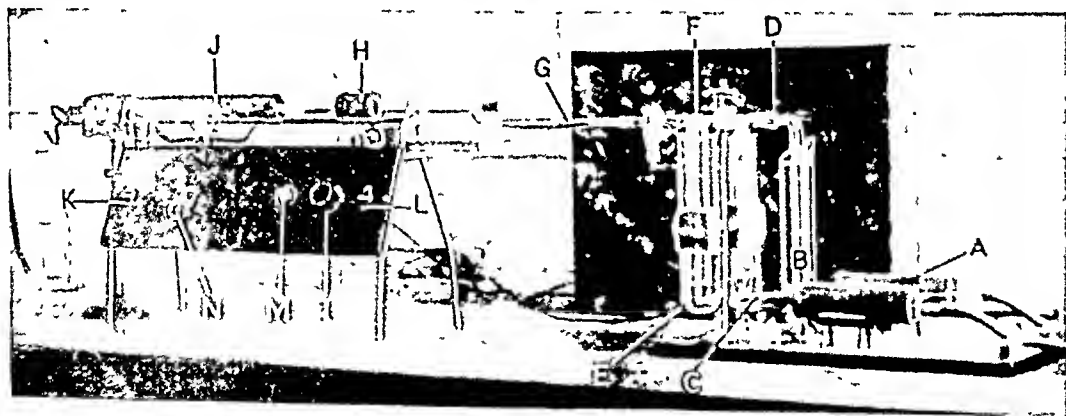


FIG. 3.

heated to 650°C. The gases are cooled by means of the water jacket, B, which is connected to the preheater tube with a ground glass joint, C, sealed with Krönig's glass cement. The top of the cooling jacket joins the pressure regulators by means of a single ground glass joint, D, with an internally sealed tube enabling the oxygen and air to be separated. The pressure regulators consist of two round-bottomed tubes, E, 150 mm. long and 55 mm. in external diameter, supported by a single brass column and held in position by metal clips. The regulation of the gas speed is effected by raising or lowering the tubes. The

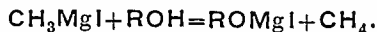
bubble counter is connected on one side via a three-way tap to the gas-bells, R, and on the other to a straight tube, G, 6 in. long, which replaces the normal U-tube; the straight tube has the advantage that the carbon dioxide absorbent, which forms a hard cake after use, is readily removed. Both these connections are made by standard ground-glass joints sealed with Krönig's cement. The pilot heating element, H, consists of a steel tube 1½ in. long and 1 in. in diameter, with a moulded London cement grid to take the heating unit. This pilot unit is heated to a maximum temperature of 750°C., which is

adjusted by means of a resistance, *I*, fitted to the panel of the combustion stand. The long burner, *J*, is 7 in. in length and is adjusted to a temperature of 700°C., with a uniformity of temperature of  $\pm 30^\circ$ . The panel of the combustion stand has two switches, one, *K*, for the main burner and the other, *L*, for the pilot. An indicator light, *M*, is connected with the pilot burner. In the centre of the panel is an indicator, *N*, for the number of halogen compounds analysed. The accuracy of this rubber-free apparatus is within  $\pm 0.1\%$ .

#### Determination of Active Hydrogen.

The method of A. Soltys for the determination of active hydrogen appears to incorporate most of the advantages of previous methods described, and in addition permits the estimation of the amount of reagent actually employed, thus permitting the quantitative determination of groups which react with the Grignard reagent without liberating methane to be carried out.

**Principle.**—The method is based upon the quantitative reaction of methyl magnesium iodide with substances containing an active hydrogen atom (*i.e.*, containing  $-\text{OH}$ ,  $-\text{COOH}$ ,  $\text{NH}$ , etc.); the methane formed is collected in a burette and measured volumetrically. The following reaction is involved:



**Apparatus.**—The apparatus, as shown in Fig. 4, consists of two parts: the methane generator, and the methanometer. They are

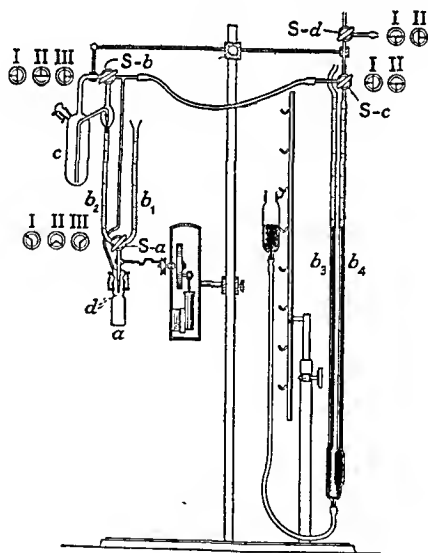


FIG. 4.

connected to each other with a rubber tubing 16 cm. long, having a bore of 3 mm. and an outer diameter of 9 mm.

The methane generator consists of the removable reaction flask (*a*), the two burettes (*b*<sub>1</sub> and *b*<sub>2</sub>), the Grignard reagent stock-flask or reagent vessel (*c*), and two three-way stopcocks, one of which is on the bottom (*S-a*) and the other on

the top (*S-b*). The Grignard reagent stock flask has a capacity of 50 ml. and is provided with a ground-glass stopper and two outlets. The outlet on the top leads to stopcock *S-b*. The outlet on the side is of capillary tubing, one arm of which extends to the bottom of the Grignard reagent vessel; the other arm leads to burette *b*<sub>2</sub>, where it forms an automatic zero-point adjustment. The reaction flask, *a*, which has a capacity of 8 ml., is attached by means of a ground-glass joint to a hollow stopper, or head. The capillary inlet tube (*d*), which may be connected either with burette *b*<sub>1</sub> or *b*<sub>2</sub>, according to the position of the stopcock *S-a*, is sealed to the latter and extends through the hollow stopper into the reaction flask. Another capillary tube leads from the hollow stopper up to the right side arm of stopcock *S-b*. Burette *b*<sub>2</sub> is graduated to 0.02 ml., and has a capacity of 2 ml.; it serves for the measurement and the introduction of the Grignard reagent. Burette *b*<sub>1</sub> is also graduated to 0.02 ml., but has a capacity of 1 ml., and is used for the introduction of the aniline. An automatic shaking device is connected to the apparatus by means of a wire attached to the capillary inlet tube.

The methanometer consists of two parallel gas burette (*b*<sub>3</sub> and *b*<sub>4</sub>), each having a capacity of 7 ml.; both are graduated to 0.02 ml. The methane burette *b*<sub>4</sub> carries two three-way stopcocks, *S-c* and *S-d*, at its upper end, which facilitate the admittance of methane and dry nitrogen, respectively. Burette *b*<sub>3</sub> is open on the top to permit establishment of equilibrium with the atmospheric pressure. Its curved bottom is sealed to burette *b*<sub>4</sub>, and is provided with an outlet which connects both burettes, by means of a rubber tubing, to the mercury leveling bulb, which is suspended from a rack having a pinion adjustment.

#### Reagents.

**Nitrogen** should be of 99.9% purity, and is used for the preparation of the reagent, as well as during the determination, to provide an inert atmosphere. Anisole and pyridine are used as solvents. Amyl ether is used as the solvent in the Grignard reagent.

**Preparation of the Grignard Reagent.**—In a 200-ml. round-bottom flask are placed 0.6 g. of magnesium, 2.5 ml. of methyl iodide, and 50 ml. of freshly distilled amyl ether. This flask is provided with a ground-glass condenser and a sealed-in inlet tube. The flask is charged through the inlet tube with nitrogen which has been dried by passing it through a wash bottle containing concentrated sulphuric acid and a U-tube filled with anhydrous. Before the start of the reaction the flow of nitrogen is reduced to about one bubble per second. Water is passed through the condenser jacket, and after starting the reaction by dropping in a crystal of iodine, the flask is heated for 2 hours on the water bath. To remove the last traces of methyl iodide the condenser outlet is connected to a suction pump, and the rubber tubing connecting it to the pump is closed with a pinch-clamp. The burner is extinguished and the water passing through the condenser jacket shut off, as is the flow of nitrogen. The pinch-clamp regulating

the vacuum from the suction pump is then slowly opened, the contents of the flask thus being caused to boil; boiling, with the aid of the suction, removes the methyl iodide completely, although a small amount of amyl ether is also lost. As soon as this pinch-clamp is fully opened, the pinch-clamp beyond the nitrogen inlet-tube is opened to let one bubble of nitrogen per second pass through the wash bottle. After 15 minutes the pinch-clamp regulating the vacuum is closed, and the one throttling the delivery of nitrogen slowly opened completely, so that the flask is again filled with nitrogen. The rubber connections are then removed and the top of the condenser, as well as the inlet-tube, closed with tight-fitting rubber stoppers or rubber tubing. It is advisable to determine the strength of the reagent before transferring it to the apparatus by dissolving about 5 ml. of the reagent in an excess of 0.1N. hydrochloric acid and titrating it back with 0.1N. sodium hydroxide. The Grignard reagent should be of 0.4-0.5M. concentration, because it becomes weaker upon transfer to the apparatus, and a reagent of less than 0.3M. concentration reduces the speed of the reaction to an undesirable extent.

**Procedure.**—The reaction flask is removed from the apparatus and cleaned with ethyl alcohol and dilute hydrochloric acid; the grease is removed from its neck with cotton wound around a notched iron wire and moistened with acetone. It is finally rinsed with acetone and dried at 100°C. The ground-glass joint of the reaction flask is also cleaned with cotton moistened with acetone. Stopcock S-a is then turned to position III and some alcohol, followed by acetone, introduced through burette  $b_1$ . Should there be a deposit of basic magnesium iodide in the capillary, it is removed with dilute hydrochloric acid. While the reaction flask and the pipette are permitted to dry in a drying block, a slow stream of nitrogen is passed through the apparatus, with the stopcocks S-d and S-c in position I; air is drawn through capillary  $d$  at the same time to dry burette  $b_1$ , and after 5 minutes the apparatus is ready for the determination.

Enough substance is weighed in the long-stem charging tube to yield about 1 ml. of methane, and transferred to the still warm reaction flask. With the warm pipette 0.5 ml. of anisole, or another solvent, such as pyridine, is added; then the flask is attached, stopcocks S-d, S-c, S-b turned to position I, S-a to position III, and nitrogen passed through the apparatus. The reaction flask is immersed in water at room temperature and shaken to bring about equalisation of temperature. (The charging tube is reweighed during this time, because this procedure permits the immediate attachment of the still warm reaction flask to the apparatus.)

If the substance does not dissolve during the shaking, the reaction flask is heated to 100°C. by placing it on the heating block, and it should be noted whether the substance precipitates again after cooling. After 10 minutes the temperature has become equalised, and burette  $b_2$  is filled with the reagent. Gas burette  $b_4$  is adjusted to the zero point, and first stopcock

S-c, then S-a, turned to position I, and about 0.5 ml. of reagent, or an excess over the theoretical amount, run into the reaction flask. The mercury bulb is lowered about 5 cm. and the reaction flask shaken for 5 minutes, after which time burette  $b_2$  and gas burette  $b_4$  are read. The blank volume and the volume of reagent added are deducted to obtain the volume of methane formed by the substance. The reaction flask is then immersed in boiling water and the shaking continued for 10 minutes, because many substances react quantitatively only when heated. The mercury bulb remains lowered during this time to create a slight under-pressure. The hot water is then replaced by water at room temperature, the reaction flask shaken for another 10 minutes, and gas burette  $b_4$  read again. Burette  $b_1$  is then filled with aniline, of which about 0.7 ml. is run into the reaction flask; the flask is shaken for 5 minutes, with the mercury bulb again lowered about 5 cm. The volume of the added aniline is then deducted from the increased gas volume, and the blank added to obtain the volume of methane corresponding to the amount of unused reagent. The time required for the entire analysis, including the weighing of the substance, is about one hour.

#### LITERATURE ON DETERMINATION OF ACTIVE HYDROGEN.

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W. F. B.

**MICROCLINE.** A triclinic potash-felspar similar to orthoclase in composition,  $\text{KAlSi}_3\text{O}_8$ . It almost invariably contains sodium, and may include small quantities of cesium, rubidium, and calcium. Characterised by two types of multiple twinning crossing each other nearly at right-angles to produce microscopic cross-hatching or grating. Possesses a perfect basal cleavage almost perpendicular to a good side pinacoidal one. Colour white, or tinted by impurities to cream-yellow or red; bright green microcline is known as *amazonstone*.  $\rho$  2.56, hardness 6. In contradistinction to orthoclase, microcline shows no inversion and remains unchanged up to its melting-point. When it encloses discontinuous bands of the soda felspar, albite, it is called microcline *perthite*, or *micro-perthite* if the bands are very fine. Microcline is not common in volcanic rocks, but is often the main felspar in granitic pegmatites, in which it may occur as enormous crystals. In Karelia, U.S.S.R., a mass weighing over 2,000 tons had the optical continuity of a single crystal.

The felspar of commerce, often called orthoclase, probably consists largely of microcline or an intergrowth of microcline and plagioclase.

It is used in ceramics for the manufacture of pottery, both in the body of the ware and in the glaze, and is employed in the glass industry to contribute alumina to the glass batch. Some of the purest felspar is used in making artificial teeth, and the lower grades find much service in the preparation of floor tiles, enamels, scouring soaps, binders for abrasive wheels, and paint fillers. The annual world production of ground felspar is about 500,000 tons, of which the United States yields nearly two-thirds.

D. W.

#### MICROCOSMIC SALT (v. Vol. II, 548c).

**MICROLITE.** Essentially a pyrotantalate of calcium, but containing also niobium, sodium, and subordinate amounts of other elements;  $(\text{Na}, \text{Ca})_2\text{Ta}_2\text{O}_6(\text{O.OH}, \text{F})$ . With increasing niobium it passes gradationally into *pyrochlore*,  $\text{NaCaNb}_2\text{O}_6\text{F}$ . Typical analyses show that microlite includes  $\text{Ta}_2\text{O}_5$  73,  $\text{CaO}$  11, and  $\text{Na}_2\text{O}$  2.3% (approximately), with up to 4.2% of  $\text{UO}_2$ . Usually crystallises as octahedra, often of minute size, hence the name. Colour pale yellow to brown, with a resinous lustre, the darker varieties transmitting light only in thin splinters.  $\rho$  5.1–6.4, hardness  $5\frac{1}{2}$ . Slowly decomposed by concentrated sulphuric acid and readily by fused potassium bisulphate. A somewhat rare mineral typically found in granite pegmatites, frequently associated with tantalite and columbite. Observed as an alteration product of tapiolite,  $\text{FeTa}_2\text{O}_6$ .

Reference.—C. Palache, H. Berman, and C. Froudel, "Dana's System of Mineralogy," 7th ed., Vol. I, New York, 1944, p. 748.

D. W.

#### MICRO - ORGANISMS, GROWTH FACTORS FOR.

##### I. CONCEPTION AND HISTORY OF GROWTH FACTORS.

The term "growth-factor" is used when speaking of micro-organisms in the same sense as the word "vitamin" in connection with animal nutrition. With increasing knowledge of the chemical structure of individual vitamins and growth-factors, it has become clear that neither term denotes a chemical class or a category of biologically active substances. These names are a transient convenience for referring to essential constituents of an adequate diet which have hitherto escaped identification, while they still remain unknown except by the effects of their absence, namely the failure of the test organism to grow normally. When one of these substances has been identified chemically, it no longer serves a useful purpose to classify it as a vitamin or growth-factor; what is then important is its physiological function and the mechanism of its action.

The conception of growth-factors in the nutrition of micro-organisms is now being replaced by a broader view which sees these substances as part of a wider class of *essential metabolites*.<sup>18, 19, 34, 110</sup> These are components of metabolic reactions which are common to very different types of living organisms. There is an underlying unity in biochemistry, in that many of the biochemical reactions which make up the metabolic processes of growth are basically the

same in otherwise very different kinds of organisms. These metabolic processes are the chains of co-ordinated biosynthetic reactions and their complementary energy-yielding reactions which are the means of building up the new living matter produced in growth. The essential metabolites may be substrates in some of these chains of enzyme reactions, or components of the enzyme systems, etc. Thus aneurin, riboflavin, pyridoxin, and nicotinic acid, which are all growth factors for numerous micro-organisms, are essential metabolites in the sense used here; they are undoubtedly used, at least in part, by the micro-organisms which require them as growth factors, in order to form part of co-carboxylase and aneurin-protein enzymes, flavo-protein enzymes, the co-enzyme of tyrosine decarboxylase and co-enzymes I and II, respectively. The substances which particular species or strains require as *nutrients* reflect their abilities to synthesise these essential metabolites for themselves; where the synthetic powers of an organism are more restricted the essential metabolites which are required as nutrients will be correspondingly greater in number and complexity. Owing to this common biochemistry of essential metabolic processes the discovery of a growth factor for one organism gives information about essential metabolic processes common to many organisms. Thus the earlier studies of vitamins in animal nutrition, and of growth factors, etc., in the nutrition of bacteria, yeasts, lower fungi, and protozoa, which were originally carried out independently, are now found to be closely connected because of the common usage of similar metabolic reactions in the growth processes of all these types of organism.<sup>20, 34, 47, 64, 73</sup>

**Nutritional Studies.**—The investigation of this field has largely proceeded from the angle of nutritional studies, because the reaction to the absence of an essential nutrient, namely failure of normal growth, provides a suitable test-object for tracing a biologically active substance. The study of the exact nutritional requirements of micro-organisms has proceeded by an analytical approach similar to that used in the study of animal nutrition: the fractionation of complex nutrient media of empirical composition upon which the given micro-organism will grow *in vitro*. This leads to the replacement of various fractions of the diet by known substances, to form a deficient basal medium which supports the growth of the organism under investigation only when a further addition, e.g., a tissue extract such as a protein-free liver or yeast extract, is made. This extract then contains all the additional, and initially unknown, compounds which the given organism requires for normal growth. These additional unknowns would be referred to as "growth factors" until identified. This identification may consist in fractionation and purification until the biologically active substance present is recognised as a known compound, or in the isolation and the determination of structure of a new compound.

##### HISTORICAL.

Brief historical reference may be made to the development of this field. Quite early attempts were made to grow various types of micro-



organisms in media of completely known composition. Many apparent successes were later found to be erroneous owing to lack of appreciation of the minute quantities of substances which were adequate to permit easily observable amounts of growth, especially with yeasts and bacteria. Not until this was recognised and rigorous methods of working were adopted could assured advances be made in the exact analysis of nutrient needs.

**Bacteria.**—Winogradsky,<sup>11c</sup> *see* <sup>32</sup>, the discoverer of the chemosynthesising autotrophic bacteria, grew these organisms in simple mineral media. This was possible because of the special type of metabolism, involving highly developed synthesising powers, which is characteristic of this type of bacteria. For example, carbon dioxide can be used as sole source of carbon, and nitrate or nitrite as sole source of nitrogen, by certain of these organisms; more complex organic compounds are not required by them as nutrients.<sup>58, 59</sup> But attempts to use almost equally simple media for heterotrophic bacteria with a carbohydrate (glucose) as source of carbon and energy, and ammonium salts or asparagine as source of nitrogen, together with various salts, had limited success for reasons which only subsequently became apparent. The school of Braun, from 1920, onwards,<sup>6</sup> was successful in cultivating certain organisms of the *Salmonella* group, and similar "enteric" organisms, in chemically defined media of simple composition, but it became evident from this and other work that even within these species (*Eberthella typhosa*, *Salmonella*, organisms of the dyscutery group, etc.) only some strains—named "non-exacting"—had simple nutrient requirements; other "exacting" strains of the same species required more complex nutrients.<sup>6</sup> In some cases the more exacting nutritional requirement could be supplied by a mixture of amino-acids, in place of ammonia or a single amino-acid.<sup>21</sup> (The exact amino-acid requirements of many bacteria have now been studied; this topic is omitted from this article.)

There are numerous species of bacteria now known to be able to grow on simple media of this kind, and not requiring any special addenda. But from the point of view of the development of the field of study this mode of approach was unable to extend far, and most of the subsequent development of bacterial nutrition proceeded by the analysis of complex empirical media. This method of approach was inevitable in the case of bacteria of which the nutritional requirements are very complex; this includes many of the bacteria pathogenic to man and animals. Observations which strikingly drew attention to the complex nutrition of many species of bacteria came from attempts to cultivate John's bacillus and *Haemophilus influenzae* (Pfeiffer's bacillus) *in vitro*. It was found impossible to cultivate John's bacillus on the ordinary media of bacteriology until Twort and Ingram<sup>99</sup> showed that some special substance, which was synthesised by other members of the class of acid-fast bacilli, had to be incorporated in the medium before John's bacillus could grow. Ordinary complex bacteriological media did not contain this substance. Similarly heat-

sterilisation of the usual type of complex medium, *e.g.*, peptone-broth, destroyed a substance required by *Haemophilus influenzae*.<sup>70</sup> Therefore by heat-sterilisation of such a medium, a deficient basal medium was inadvertently prepared which could be used to test for the presence of this heat-labile substance in tissue-extracts, etc. This labile growth-factor was named the V or vitamin factor; as this name shows, it was detected at a time when the vitamins of animal nutrition were already differentiated as objects of biochemical study. Its properties were studied,<sup>11, 77</sup> and it was finally identified as a pyridine nucleotide, either co-enzyme I or II being interconvertible in the organism.<sup>49, 56</sup>

From about 1925 many premature attempts were made to implicate the vitamins of animal nutrition in the nutrient requirements of micro-organisms; but the function of vitamins was not proved until vitamin-B<sub>1</sub> (anerin) had been isolated in a pure state. It was then possible to show, unequivocally, that anerin was an essential nutrient for a micro-organism. This was first done by Schopfer<sup>76</sup> for the mould *Phycomyces blakesleeana*. Shortly after, Tatum, Wood, and Peterson<sup>93</sup> showed that anerin was essential for certain lactic-acid bacteria. When riboflavin and, much later, pyridoxin, were isolated, these were also shown to be nutrients required by certain species of bacteria and other micro-organisms (*see* Section II).

A survey made in 1936<sup>32</sup> showed that bacteria as a whole exhibited the very widest range of complexity of nutritional requirements, extending from the chemosynthesising and photosynthesising autotrophic bacteria with the very simplest nutrient needs, to saprophytic and pathogenic heterotrophic species having a very complex nutrition. All degrees of nutritional complexity could be observed. Lwoff<sup>46</sup> had outlined similar conceptions for protozoa. Subsequent developments have caused no radical changes in the conceptions developed in those two reviews; but knowledge acquired since then has supplied much fuller information.<sup>34, 47</sup> The major development has come in the identification of numerous growth-factors (essential metabolites) which are required by the bacteria the nutrition of which is complex.

**Yeasts.**—From the time of Pasteur yeasts had been cultivated in what were sometimes thought to be media of simple known composition, but Wildiers'<sup>104</sup> study focussed attention on the exact nutrient requirements of this type of micro-organism. Wildiers proposed "bios" as the name for unidentified material which he showed to be required in addition to the known components of the simplified culture media he used. From that time much study was devoted to the so-called "bios problem." This eventually led to the recognition that yeasts, too, differed in the complexity of their nutrient requirements, this complexity reflecting the ability of different strains to synthesise one or more of the essential metabolites which were eventually identified by studies similar to those described above for bacteria.<sup>105</sup> Eastcott<sup>13</sup> showed that inositol was required by some yeasts. Subsequently  $\beta$ -alanine,<sup>107</sup> panto-

themic acid,<sup>106</sup> and biotin<sup>29, 36, 101</sup> were all first observed as growth factors in connection with yeast growth. Later these compounds were implicated in the nutrition of other types of organism (bacteria, lower fungi, protozoa, and higher animals). This led to a fusion of nutritional studies in general. Since about 1930 intensive study of the exact nutrient requirements of many different species of bacteria, yeasts, lower fungi, and protozoa has been widely developed. This has led to:

- (i) The discovery of new compounds, e.g., biotin and pantothenic acid.
- (ii) The finding that certain compounds already known to organic chemistry are required as essential nutrients for various organisms, e.g., nicotinic acid and the pyridine nucleotides, uracil (and other pyrimidines and purines), glutamine, pimelic acid, inositol,  $\beta$ -alanine, choline, and *p*-aminobenzoic acid.
- (iii) The finding that a compound first identified as a nutrient for one species may also be required by other species of the same or different types of organisms (see Section II).
- (iv) The finding that species of micro-organisms which do not need one of these substances as a nutrient will usually be found to synthesise it. Evidence of the latter kind supports the interpretation of the rôle of this synthesis as supplying, endogenously, an essential metabolite, which has to be acquired from external sources if the organism cannot synthesise it. In the latter case it appears as a nutrient requirement or growth factor.

In Section II is given a list of substances which are essential metabolites in the sense used in this article, with representative organisms showing different abilities in synthesis. In reading the tables it must be remembered that, owing to the flexibility of micro-organisms with regard to biosynthesis, the examples given are not fixed and exclusive. Strains of a given species may be found which have greater or lesser synthetic powers than those hitherto examined, and hence may have correspondingly less or more complex nutrient requirements in culture than those already known.

In the case of lower fungi, such as *Neurospora*, recent observations on X-ray-induced mutants show that very simple genetic changes, often involving only one gene, may result in the mutant becoming unable to perform a biosynthesis which the normal parent organism can perform. The deficient mutant then becomes dependent on finding an external source of the substance which it cannot synthesise. Thus mutants unable to synthesise *p*-aminobenzoic acid, choline, pyridoxin, inositol, tryptophan, etc., have been observed.<sup>1, 14, 30, 89, 92, 94, 95</sup>

The study of these genetically controlled nutritional differences will undoubtedly be important in the study of the metabolic processes involved.

## II. GROWTH-FACTORS REQUIRED BY MICRO-ORGANISMS.

In the following list references are given for representative groups of micro-organisms: bacteria, yeasts, lower fungi, and protozoa. The growth factors are grouped under the respective essential metabolite molecules, of which a growth factor may be a part. To limit the size of the bibliography, in many cases the more recent original publications and reviews are listed, from which references to earlier original publications can be obtained. It is to be remembered that this field is developing rapidly at the present time (see<sup>34</sup>), and the bibliography is in no way comprehensive.

**Aneurin** (v. Vol. I, 371c, 583b).—(The pyrimidine moiety = 2-methyl-5-X-methyl-6-aminopyrimidine, where X=some substituent such as Br, NH<sup>2</sup>, OH, etc. The thiazole moiety = 4-methyl-5- $\beta$ -hydroxyethyl thiazole).

The specificity of the aneurin molecule in the nutrition of micro-organisms has been widely studied.<sup>35, 47, 83</sup>

*The intact aneurin molecule is required as growth-factor:*

Lower fungi: species of *Phytophthora*.<sup>68</sup>

Protozoa:<sup>27</sup> *Glaucoma pyriformis*,<sup>47</sup> *Strigomonas*.<sup>49</sup>

*The pyrimidine and thiazole moieties are together required:*

Bacteria: *Staphylococcus aureus*, *Staph. albus*<sup>33, 65</sup>; *Salmonella gallinarum*<sup>81</sup>; propionic acid bacteria<sup>81</sup>; *Cl. tetani*<sup>16</sup>; *Strept. lactis*.<sup>60</sup>

Lower fungi: *Phycomyces blakesleeanus* and *Ph. nitens*; *Ustilago scabiosa*.<sup>68</sup>

Protozoa.<sup>27, 47, 49</sup>

*Only the pyrimidine moiety required:*

Lower fungi: *Sclerotium delphinii*, *Pythium polycladon*, *Phytophthora jagopyri*<sup>68</sup>; formation of perithecia of *Melanospora destruens*<sup>28</sup>; *Rhodotorula flava*, *Rh. rubra*.<sup>68</sup>

*Only the thiazole moiety required:*

*Mucor ramannianus*.<sup>63</sup>

Protozoa.<sup>27, 47, 49</sup>

**Riboflavin** (v. Vol. VI, 91a). Specificity.<sup>124</sup>  
Bacteria: haemolytic *Streptococci*<sup>113</sup>; *Streptococcus fecalis*<sup>115</sup>; *Enterococci*<sup>60</sup>; *Cl. tetani*<sup>16</sup>; lactic and propionic acid bacteria. Some strains synthesise riboflavin slowly and growth is stimulated by its addition as nutrient; strains have been deliberately trained to synthesise.<sup>86, 87, 109</sup>

**Pyridoxin**. Specificity.<sup>4, 69</sup>

Bacteria: species of lactic acid bacteria<sup>4, 42, 85</sup>; *Streptococci*<sup>63, 78, 113</sup>; *Enterococci*<sup>60</sup>; *Cl. tetani*.<sup>16</sup>

Lower fungi: *Ceratostomella ulmi* and related species<sup>68</sup>; *Neurospora* mutant "pyridoxinless."<sup>89</sup>

Yeasts: in yeast growth pyridoxin is important; its relative importance as a growth factor is related to the ability to synthesise, which in turn is related to the character of the particular strain and to the other cultural conditions.<sup>12, 54, 77, 105</sup> *Pyridoxamine* and *pyridoxal* (the amine and aldehyde, respectively, corresponding to pyridoxin) are more active than pyridoxin



with some bacteria,<sup>83</sup> probably because they represent higher stages in the synthesis of the co-enzyme of tyrosine decarboxylase, which appears to be a phosphorylated derivative of pyridoxamine.<sup>26</sup>

**Pantothenic Acid.**—The two portions of this peptide,  $\beta$ -alanine and pantoic acid (lactone) (=  $\alpha$ -hydroxy- $\beta\beta'$ -dimethyl- $\gamma$ -butyrolactone) are sometimes sufficient singly as growth factors (cf. Aneurin, above). Specificity.<sup>55, 90, 113</sup>

**Complete pantothenic acid molecule required** (sometimes the 2 separated portions together will function):

Bacteria: some strains of *C. diphtheriae*<sup>57</sup>; lactic-acid bacteria<sup>42, 62</sup>; propionic acid bacteria<sup>97</sup>; *Streptococci*<sup>78, 82, 90, 113</sup>; *Pasteurellae*<sup>2</sup>; *Cl. tetani*<sup>16</sup>; *Enterococci*<sup>60</sup>; *Cl. welchii*<sup>91</sup>; *Proteus morganii*.<sup>61</sup>

Lower fungi: *Neurospora* mutant.<sup>1</sup>

Yeasts<sup>105, 106</sup>.

$\beta$ -Alanine required:

Strains of *C. diphtheriae*.<sup>57</sup>

Yeasts.<sup>105, 106</sup>

**Pantoic acid (lactone) required:**

Bacteria: *Acetobacter suboxydans*<sup>100</sup>; *Streptococcus haemolyticus*.<sup>111</sup>

**Pyridine Nucleotides.**—Specificity.<sup>75</sup>

Bacteria: species of *Haemophilus* group.<sup>47, 48</sup>

**Nicotinic Acid** (v. this Vol., p. 479). Specificity.<sup>35, 38, 47, 56</sup>

Bacteria: *Staph. aureus*<sup>33, 35</sup>; *Proteus vulgaris*<sup>47, 56, 74</sup>; *Proteus morganii*<sup>61</sup>; lactic-acid bacteria<sup>83, 96</sup>; dysentery bacilli<sup>74</sup>; *C. diphtheriae*<sup>57</sup>; *Acetobacter suboxydans*<sup>100</sup>; *Leuconostoc mesenteroides*<sup>24</sup>; *Cl. tetani*<sup>16</sup>; *Enterococci*.<sup>60</sup>

Yeasts.<sup>105</sup>

Nicotinamide is required by certain *Pasteurellae*, which cannot use the acid.<sup>2</sup> Many organisms requiring nicotinic acid as growth-factor have been shown to synthesise pyridine nucleotides.

**Biotin.**

Bacteria: *Rhizobia*<sup>108</sup>; *Clostridia*<sup>16, 32</sup>; lactic-acid bacteria<sup>42, 80, 83</sup>; *Brucellae*<sup>35a, 50, 51</sup>; *Pneumococci*.<sup>25</sup>

Lower fungi: *Ashbya gossypii*<sup>68</sup>; *Melanospora destruens*.<sup>23</sup>

Yeasts<sup>29, 105</sup>; Osmophilic *Zygosaccharomyces*.<sup>45</sup>

Biotin is sometimes slowly synthesised and growth is then stimulated by its addition to media.<sup>23, 37, 65, 108</sup>

**Pimelic Acid.**—This compound may be a precursor of biotin in biosynthesis by some organisms<sup>102</sup>; it is a nutrient required by certain strains of *C. diphtheriae*.<sup>57</sup>

**p-Aminobenzoic Acid.**—Required as growth factor:

Bacteria: *Cl. acetobutylicum*<sup>39, 71, 72</sup>; *Cl. thermosaccharolyticum*<sup>9</sup>; *Acetobacter suboxydans*<sup>40, 41, 100</sup>; *C. diphtheriae* strain Dundee<sup>8</sup>; *Lactobacillus arabinosus*.<sup>44</sup>

Lower fungi: *Neurospora* mutant "amino-benzoicless." <sup>95, 98</sup>

**Glutamine** (v. Vol. VI, 37b). Specificity.<sup>52</sup>

**Required as growth factor:**

Bacteria: haemolytic *Streptococci*<sup>3, 15</sup>; lactic-acid bacteria<sup>15, 64</sup>; various.<sup>22</sup>

**Purines and Pyrimidines.**—A number of purines and pyrimidines, singly or together, are

important in bacterial nutrition, as growth stimulants or essentials. It is not yet clear what rôle they play, and their effects are often related to the presence of other constituents of the medium.

**Uracil** is a growth factor for: anaerobic growth of *Staph. aureus* (but is synthesised in aerobic growth)<sup>66</sup>; *Cl. tetani*<sup>16</sup>; *Streptococcus salivarius*<sup>82</sup>; lactic-acid bacteria.<sup>84</sup>

For Adenine (v. Vol. I, 141b), Guanine (v. Vol. VI, 150c), Hypoxanthine (v. Vol. VI, 408b), Xanthine, and Thymine effects, see<sup>43, 67, 82, 84</sup>.

**Inositol** (v. Vol. VI, 491a).

Yeasts.<sup>13, 105, 112</sup>

Lower fungi: *Ashbya gossypii*<sup>6, 7, 68</sup>; *Trichophyton discoides*<sup>70</sup>; *Neurospora* mutant.<sup>1a</sup>

**Choline** (v. Vol. III, 92d).

Bacteria: *Pneumococcus*.<sup>25</sup>

Lower fungi: *Neurospora* mutant.<sup>30</sup>

**Oleic Acid.**—*C. diphtheriae*<sup>10</sup>; *Cl. tetani*.<sup>16</sup>

**2-Methyl Naphthaquinone.**—Effect on John's bacillus.<sup>114</sup>

**"Folic Acid."**—Structure at present unknown; originally detected as required for *Streptococcus lactis* R.<sup>55</sup> and is involved in the nutrition of other organisms.

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MICROPHYLLIC ACID (v. Vol. VII, 295a).

## MICROSCOPE, ELECTRON.

## 1. DUAL THEORIES OF LIGHT AND ELECTRONS.

The present century has been a revolutionary period in the study of physics. By 1900 physicists were fairly certain of the truth of the wave theory of light, as represented in Maxwell's Electromagnetic Theory, and they spoke in very familiar terms of the "æther of space." However, with the discovery of the photoelectric effect and Planck's theoretical treatment of the laws of radiation, suspicion that all was

not well with the wave theory arose. By 1910 all the physicist was prepared to assert was that for some experimental results, such as interference and diffraction, the wave theory alone offered an acceptable explanation; for other phenomena, such as the photo-electric effect, a corpuscular theory alone was applicable.

Statements almost the converse of the above may be made regarding the theory of electrons. The electron was discovered in 1896 as a small negatively charged particle of mass about one two-thousandth of that of the hydrogen atom. Although there was considerable discussion at first as to whether a beam of electrons had the properties of a beam of light or those of a stream of particles, by 1900 the particle view held the field.

In spite of the fact that the dual theory of light was established by 1900, it was not until 1923 that de Broglie<sup>1</sup> definitely suggested that electrons might be looked upon as having a wave property as well as a corpuscular discreteness. He even suggested a formula for the wave-length to be attached to a homogeneous stream of electrons, viz.  $\lambda = (12.24 \times 10^{-8}) / \sqrt{V}$  cm., where  $V$  is the difference of potential in volts in the field through which the electrons gain their velocity.

## 2. EXPERIMENTAL PROOF OF THE WAVE PROPERTY OF ELECTRONS.

The theory of de Broglie<sup>1</sup> was substantiated a few years later by experiments carried out by Davisson and Germer<sup>2</sup> at the Bell Telephone Laboratories in New York City and, independently, by Professor G. P. Thomson,<sup>3</sup> then in the University of Aberdeen. These experiments demonstrated that a beam of electrons showed diffraction phenomena quite analogous to those of visible light and X-rays.

The question arose immediately whether an electron beam would lend itself to some form of microscopic vision (or photography). Such a result had never been obtained with X-rays, but, nothing daunted, physicists began to devise something which would give for an electron beam what glass lenses provided for light beams. The urge behind such investigation is made apparent when the impasse which had been reached in ordinary microscopy is considered.

## 3. THE DEVELOPMENT OF THE MICROSCOPE.

The ordinary compound microscope had reached a high degree of development by 1870, and it had been clearly shown that the limit in the resolving power (or in the useful magnification) had been reached. This limit is set by the fact that light shows diffraction effects, phenomena common to all forms of wave motion.

It was established theoretically by various physicists, in particular by Lord Rayleigh, that the shortest possible distance ( $\epsilon$ ) between two points on an object which can be shown as separate in the image formed by any microscope is given by the formula  $\epsilon = \lambda / 2n \sin A$ , where  $\lambda$  is the wave-length of the light used, and  $n \sin A$  is the numerical aperture (N.A.) of the objective system. This formula may also be taken to

stand for the diameter ( $\epsilon$ ) of the smallest particle which could be revealed by a light microscope. This gives for the limiting diameter of a spherical particle, which can be observed by a light microscope, a value of about  $2 \times 10^{-5}$  cm.,  $1/125,000$  in., or  $0.2\mu$  (micron).

Many attempts have been made to extend this lower limit. In 1900 the ultra-microscope was devised by Zsigmondy and Siedentopf,<sup>4</sup> but the method of illumination, which is really the "ultra-part," of the instrument, reveals only the presence of particles and tells nothing of their shape or size.

Again, the shorter is  $\lambda$ , the wave-length of the light used, the smaller is  $\epsilon$ , i.e., the smaller the particle which can be revealed. Gye and Barnard in 1925 constructed a very elaborate microscope for the use of ultra-violet light, and were able to photograph particles smaller than any already revealed, as to size and shape, up to that time.

Graton and Dane<sup>5</sup> have shown, by the use of plane, unetched surfaces of minerals as specimens, that the performance of the best objectives is rather better than the previous theory would suggest; but as most microscopical work is done with specimens which do not even approximate to an optical plane, the resolving power in actual practice does not reach that attained by Graton.

## 4. ELECTRON WAVE LENGTHS.

Although de Broglie deduced his expression for the wave-length to be attached to an electron beam [ $\lambda = (12.24 \times 10^{-8}) / \sqrt{V}$  cm.] purely from theoretical considerations, experiments performed since have tended to confirm his conclusions. Since  $V$  is the potential in volts through which the electrons are accelerated, if  $V$  is 400 v.,  $\lambda$  comes out to be  $0.6 \times 10^{-8}$  cm., a value only  $1/10,000$ th of that of light in the visible part of the spectrum. If such values of  $\lambda$  could be used for microscopical observation, the limit of  $\epsilon$  should be reduced to  $1/10,000$ th of that possible with visible light.

## 5. ELECTRON LENSES.

In the development of the dual theory of the electron, de Broglie demonstrated that the path of an electron, its so-called trajectory, as it moves through space, bears the same relation to its wave property as the ray of light does to the wave property of light. Just as the path of light is traced through a series of lenses, the refractive media, in order to determine the image of an object, so if the paths of electrons could be directed, it might be possible to focus electrons arising from an object to make them form an image. This has been accomplished by the use of either electric fields or magnetic fields; both electrostatic electron lenses and magnetic electron lenses have been produced.

(a) **Electrostatic Electron Lens.**—A simple example of the regular way in which an electron path may be deflected in an electric field is shown in Fig. 1.<sup>6</sup>

The plate A is maintained at a potential of +500 v. and the plate B at a potential of +1,500 v.; the dotted lines show the distri-

bution of the lines of equal potential, and the heavy line, *op*, shows the path of the electron.

That there is here a phenomenon to which the term "refraction" might well be applied is quite apparent when Fig. 1 is compared with one which illustrates the phenomenon of refraction of light through the atmosphere, and shows why the sun can be seen for some time after it has set.

The electrostatic electron-lens is very simple—merely a hole or aperture in a metal plate. In Fig. 2, *F* is a cathode, the source from which

electrons shoot out as indicated by the small arrows, *B* is a metal plate with a hole in the centre, and *C* a second metal plate. The plate *A* acts as a shield to the cathode *F* and, as represented here, *F*, *A*, and *B* are maintained at the same potential (zero) while *C* is at a potential of +100 v. The broken lines represent the lines of equipotential. At the opening in the plate, *B*, the electrical field is distorted as indicated by the bulging of the equipotential lines, and the paths of the electrons are refracted as they are in Fig. 1. As a result, electrons coming

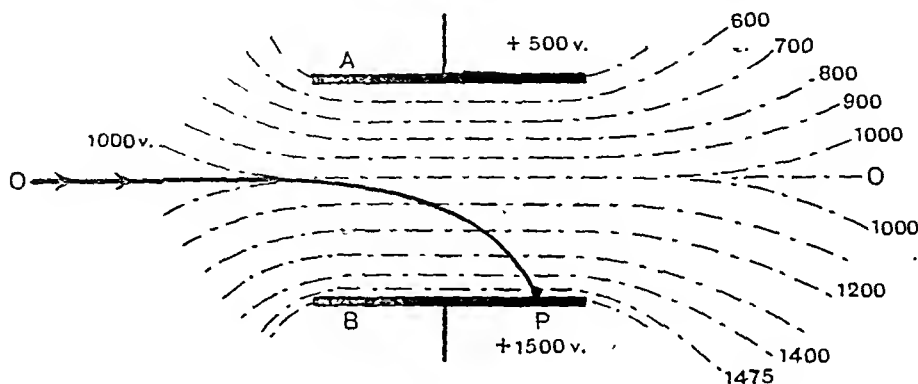


FIG. 1.

How the path of an electron bends in a potential field.

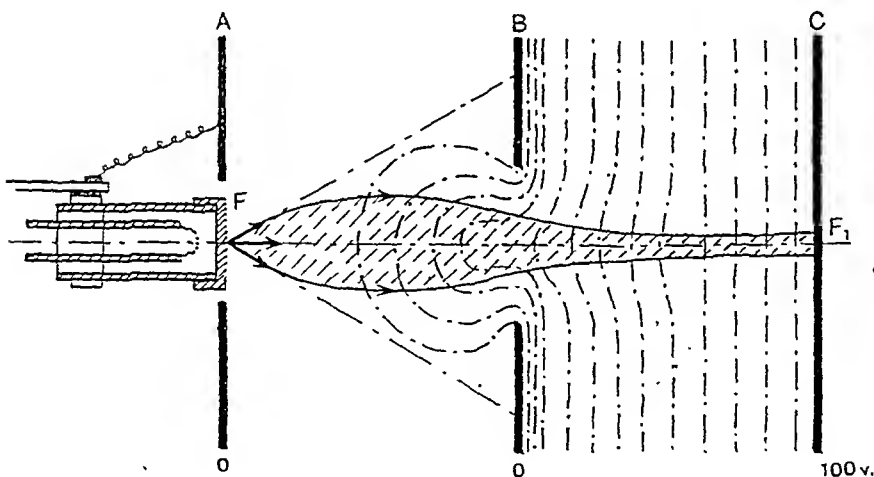


FIG. 2.

The influence of an electrode with an aperture near the cathode.

from a small area at *F* are focussed at the small area *F*<sub>1</sub> on the plate *C*.

(b) **Magnetic Electron Lens.**—The analogous case of "refraction" in a magnetic field is not quite so simple as that in an electric field.

When electrons were first discovered they were described as small, negatively charged particles, on account of the action of a magnetic field on the fluorescent beam in a vacuum tube; the path of the beam is marked by a glow caused by ionisation of the gas by the electrons, which are themselves invisible. When a magnet is

held so that the magnetic force is at right-angles to the electron beam, the latter moves as though it were a conductor bearing negative electricity in the direction of motion of the electrons. This deflection of the beam is at right-angles to both the direction of motion of the electrons and the direction of the magnetic field. This is demonstrated in Fig. 3.

There are three characteristics of the interaction of electrons and magnetic fields:

1. A magnetic field has no effect on an electron at rest.

we may resolve this velocity into two component velocities: (a) that at right-angles to the field and (b) that parallel to the field. The first component determines the circular motion in a plane perpendicular to the axis, and the second component carries the electron along the axial direction to the right only. By combining these two motions, it can be shown that electrons shooting out in directions making small angles with the axis from a point  $P$  will describe a spiral path to another point  $P_1$  on the axis; or  $P$  and  $P_1$  are analogous to object point and image point.

#### 6. SIMPLE ELECTRON MICROSCOPES.

Once the principles of regulated refraction in electric or magnetic fields were successfully

mastered, the development of electron microscopes followed as an immediate consequence. The motion of the electrons is possible only in a high vacuum, and their paths cannot pass through anything but the smallest thickness of matter; fortunately electric and magnetic fields are non-material fields of force which can be maintained in a vacuum, and the electron-lens system can therefore be maintained in such a vacuum.

The first forms of the so-called electron microscopes were single electrostatic or magnetic lenses used for giving magnified images of the structure of the surface of the cathode which is used as the source of the electron stream. Very interesting pictures of the craters from which the

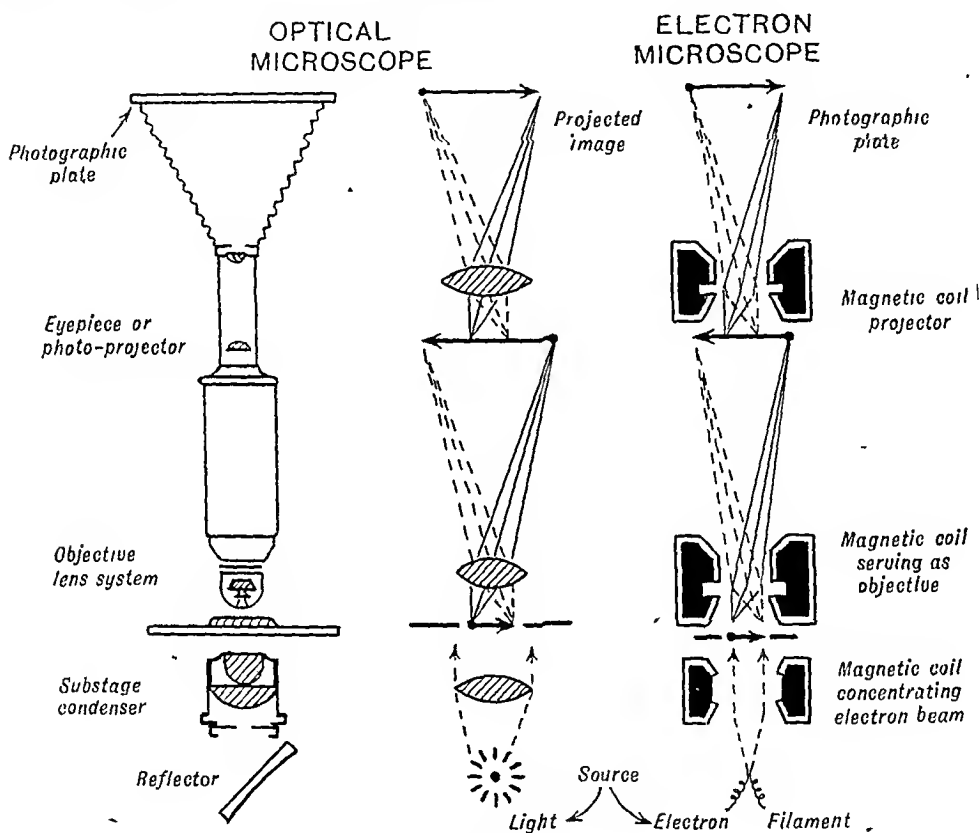


FIG. 6.

Comparison of light microscope and magnetic electron microscope.

electrons are emitted have been produced. These studies show that the sources very often wander about the surface or become exhausted from point to point on the cathode. A cathode made, for example, of nickel, is covered with barium oxide, which is the source of the electrons; after the cathode has been emitting for some time, the barium tends to be segregated along the boundaries between crystal elements (of the nickel). Consequently, important knowledge of the crystal structure of the cathode metal (nickel) can be obtained.

Again, as shown by Scott,<sup>7</sup> when organic materials are smeared on a cathode, the volatile or combustible part can be driven off by heating,

and the spots of residue on the cathode show the distribution of the metallic contents of the tissues.

Simple electron microscopes, comparable with the reading lens of ordinary optics, have been in use since about 1930.<sup>8</sup>

#### 7. THE COMPOUND ELECTRON MICROSCOPE.

The electron micrographs reproduced here were all taken with a compound electron microscope using three magnetic lenses, which served the purpose of substage condenser, objective, and projector lens, respectively. Doubtless before long similar instruments with electrostatic lenses will be developed and on the market.

The following description refers to the magnetic type of electron microscope developed at the Department of Physics in the University of Toronto.<sup>9</sup>

Fig. 6 shows diagrammatically the relation between the compound light microscope and the compound magnetic electron microscope.

The source of electrons is a filament cathode bent to a hair-pin turn; the electrons are accelerated by the electrical field between the cathode and an anode (not shown in the figure). Errors due to aberrations are minimised by having an accelerating field as large as possible; practical considerations lead to the adoption of a field of 45,000 v. as the optimum for day-to-day use. Commercial companies have experimented with much higher voltages (up to 300,000), but the gain in resolving power is more than neutralised by experimental difficulties. Whatever high voltage is adopted, it is necessary to maintain it constant to about  $\pm 3$  v.; this leads to engineering difficulties and the power regulation accounts for a considerable part of the difficulty and cost of the whole apparatus.

Another item of physical experimental difficulty is the maintenance of a sufficiently high vacuum. This requires special attention as the objects and photographic plates have to be changed frequently in the course of any investigation.

The lower magnetic coil (Fig. 6) converges the beam of electrons on the object placed just above it. The elements of the object scatter or absorb the electrons striking them, in proportion to the relative thickness and atomic properties of those elements. The electrons, which on leaving the object elements pass through the aperture in the object lens (the second magnetic coil), are focussed by the strong axially symmetrical magnetic field of this lens to conjugate image points on a fluorescent screen just below the upper magnetic coil. This screen can be viewed from the outside through a window in the wall of the microscope tube.

A fine pin-hole is bored in this fluorescent plate and the image is moved so as to bring any chosen small area of this first image over the hole. Only the electrons forming this part of the image are able to pass the plate. They are acted on by the upper magnetic coil (lens), and the final doubly-magnified image of the small section of the first image is focussed on the photographic plate.

#### 8. THE SPECIMEN HOLDER AND MOUNTING.

A special specimen holder is constructed to be slipped into the microscope through a tube inserted in the wall; it is made to fit snugly to bring the object to the proper position relative to the objective lens. Specimens such as fine fibres or edges of metal are suspended across a small hole (0.05 to 0.3 mm. in diameter) in the centre of a circular platinum diaphragm, which is held at the end of the specimen holder by a cap. For substances such as fine powder, smokes, or bacteria the material is deposited on a very thin film of collodion (about 10  $\mu$ . thick) which is stretched on a metal gauze and held across the opening of the specimen holder by a cap.

#### 9. COMMERCIAL PRODUCTION OF ELECTRON MICROSCOPE.

Siemens and Halske were offering a compound electron-microscope of the magnetic-lens type in 1938 for delivery in a year or so. The Radio Corporation of America employed L. Martin for this work, but their first commercial type, based on the University of Toronto model, was produced by Dr. James Hillier, who had joined this firm in 1940.<sup>10</sup>

In November, 1942, the Radio Corporation of America announced the marketing of a portable electron compound microscope of the magnetic-lens type.<sup>11</sup> At the same time the General Electric Company of America exhibited a portable electron compound microscope, of the electrostatic-lens type,<sup>12</sup> capable of being operated from a 110-v. power outlet. In the latter the final image is cast on a fluorescent screen and viewed from the outside; when pictures are desired the camera merely records the image on the screen, from outside. This simplifies the vacuum arrangements and so greatly reduces the cost. Commercial competition between these two types promises to bring the electron microscope within the purchasing power of even modest laboratories.

#### 10. PRACTICAL APPLICATIONS.

(a) Industrial Uses.—There is no doubt that the electron microscope will become a very important experimental instrument. At present the most useful applications seem to be in the fields of industry and medicine. In all this work there are apparent very important developments of a purely scientific nature.

1. Manufacturers of various powders—carbon blacks,<sup>13</sup> paint fillers, and rubber mixes—are interested in knowing the ultimate size of the particles in a particular preparation, as the function of these fillers depends on the area exposed by the particles. When it is realised that the material in a lump of sugar of one centimetre side (area 6 sq. cm.) will have an exposed area of several acres when broken up to particles of colloidal size, the potential immense increase in area is readily appreciated. These manufacturers are enthusiastic about information that the electron microscope has already revealed concerning the size, shape, and manner of aggregate formation of particles in powders.

2. Fibres of various materials, such as asbestos, flax, hemp, cotton, rubber, and glass offer a very extensive field for this research. There seems to be some limit to the fineness of the ultimate fibrils of natural fibres such as asbestos, flax, and cotton. New uses may be found for fibres of different materials.

3. Pictures of smokes produced by the oxides of various metals show very interesting phenomena. Some of these smokes, e.g., zinc, magnesium, and tungsten oxides, show that the finest visible particles are crystalline, while others, e.g., aluminium oxide, yield spherical particles or aggregates. It is apparent that these studies afford a fertile field for the comparison of crystalline and surface-tension forces in the formation of aggregates.

4. Pictures of the dust formed during blasting

and drilling in mines have been taken at Toronto. There is no doubt that results useful in the study of silicosis will emerge from such work.

5. Clays offer another interesting example for study, which may afford evidence as to the features of clays which are good for fillers, paper coatings, or china manufacture.

6. Particularly during the last ten years, there

#### (b) Medical and Biological Applications.

1. The most striking results in this field are those in which various viruses, formerly beyond the reach of microscopic vision, have been photographed. These include the viruses of the tobacco mosaic, small-pox, and influenza. The ability to photograph the intruder will doubtless lead to a great advance in the method of treatment of the disease.

2. Very much improved photographs have been taken of germs and bacilli, such as those of tuberculosis, which are visible in the light microscope, and it is possible that the electron microscope will enable even the life history of such minute bodies to be traced.

3. In the photograph made of the typhus germ there is a distinct indication that the germ often has attached to it a crystal, probably of some salt; this suggests that the course of the disease may bring about what might be called a "salt-anæmia" in the blood of the patient, in which case the electron microscope may help greatly in diagnosis.

4. The standard specimen used in the early development of the electron microscope was some one of the many forms of diatoms. On account of the use of diatoms as test objects for oil-immersion light microscopes, it was natural to use these shell-like structures for comparison between light and electron microscopes. In Fig. 7 are shown comparison pictures of a diatom, *Amphipleura pellucida*, as taken by (1) light of wave-length 5800 Å., (2) light <sup>15</sup> of wave-length 4050 Å., (3) light <sup>15</sup> of wave-length 3650 Å., and (4) the electron microscope. These have all been reproduced at the same magnification, approximately  $\times 11,000$ . Diatom specialists are even looking forward to finding evidence of the life history of the diatom.

#### 11. NEW DEVELOPMENTS.

In several laboratories where electron microscopes are in use, quite simple techniques for making stereoscopic photographs have been devised (see Fig. 8). The results give promise of very important additions to our knowledge. On account of the fact that the depth of focus of an electron microscope is very much greater

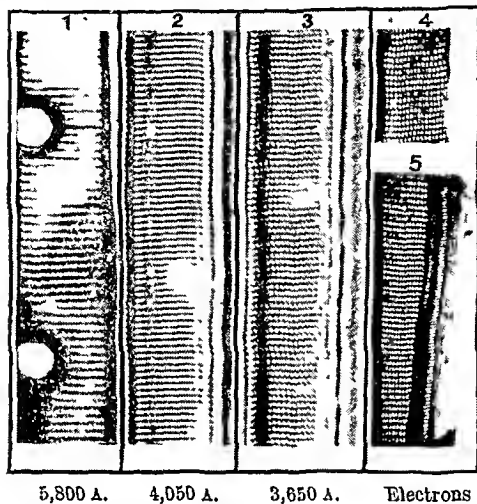


FIG. 7.

Comparison pictures of diatom, *Amphipleura pellucida*. The first three were taken with an optical microscope using different wave-lengths of light, and the last with the electron microscope

has been great development in the synthetic production of organic substitutes, as in the case of silk, rubber, and the various plastics. A knowledge of the fine structure of these materials will undoubtedly be helpful.

7. Very interesting investigations have been carried out at the Eastman Kodak Research Laboratory <sup>14</sup> on the process of development of photographic emulsions. The whole theory of this puzzling phenomenon has been re-cast in view of this work. The beginning of the process of development consists in the projection of silver fibrils out into the gelatin media from points on the sensitised crystals.



FIG. 8.

Stereoscopic view of pile of diatoms of different kinds. Magnification approximately  $\times 2,000$ .





FIG. 9.



FIG. 12.

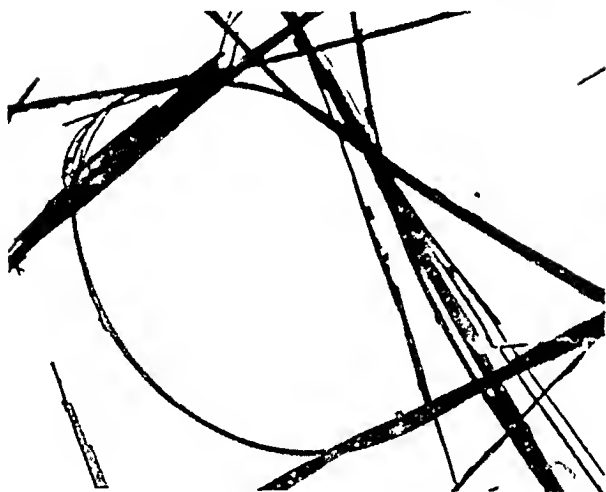


FIG. 10.

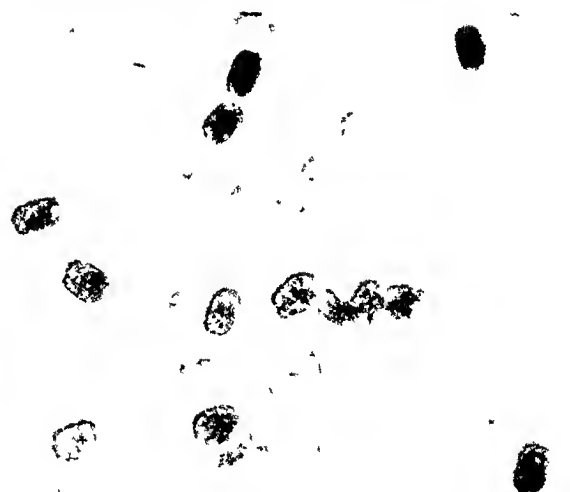


FIG. 13.



FIG. 11.

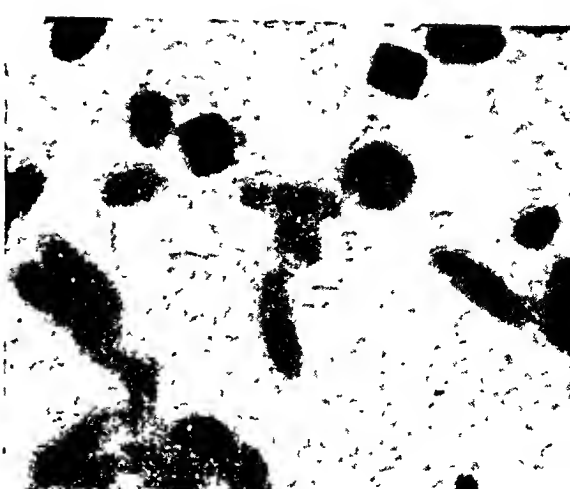


FIG. 14.



than that of the ordinary high-power light microscope, new studies of the spatial arrangement of the objects in view in the microscopic field are made possible.

The early application of the compound electron microscope was in its use in taking pictures of specimens thin enough to allow the passage of the electrons. Consequently it was not apparent that the electron microscope would be of any use in studying the surfaces of thick specimens. But even this problem has been successfully attacked in two ways: (a) by producing replicas of surfaces on thick films of material, and (b) by using the electron beam to give electron-diffraction pictures of the surface.

(a) Replicas.<sup>16</sup>—Replicas have been produced by two general methods which may be described as giving either *negative* replicas or *positive* replicas.

For negatives the surface is suffused with an organic solution which on evaporation leaves a film dried on the surface. The film is then stripped off—usually by floating it off in water. This film retains the negative of the contour of the surface on the side in contact with the surface, while the obverse of the film is plane. The negative films are thin enough for the electron beam to pass through, and the degree of absorption of the electrons shows variations in thickness of the film and thereby reveals variations in the marking of the original surface.

For making a positive, the negative is made on a thick piece of some material that can afterwards be dissolved away. This negative surface is then covered with a very thin film of some insoluble material (e.g., silver or quartz) by cathodic sputtering; on dissolving away the negative material a very thin film with a positive of the original surface is left. The degree of absorption of the electron beam again gives indications of markings on the original surface.

(b) Electron Diffraction.—The experiments on electron diffraction carried out by Davisson and Germer<sup>2</sup> and by G. P. Thomson<sup>3</sup> first confirmed experimentally the theory developed by de Broglie regarding the wave properties of electron beams.

These diffraction phenomena can be produced either by allowing the electron beam to traverse a thin film of the material, or by arranging to have the electron beam reflected from a surface of a massive solid sample. In either case direct evidence is obtained of the lattice spacing of various crystalline structures. The Radio Corporation of America<sup>17</sup> have produced a so-called "adapter" to enable the instrument to be used either for ordinary microscopical views or for electron-diffraction pictures.

The plates on p. 91 are two of asbestos fibres ( $\times 7,680$ ) (Figs. 9 and 10), iron oxide ( $\times 23,700$ ) and aluminium oxide ( $\times 22,680$ ) smokes (Figs. 11 and 12), small-pox virus ( $\times 39,600$ ) (Fig. 13), and typhus (*Rickettsia*) germs ( $\times 19,240$ ) (Fig. 14).

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E. F. B.

#### MIERSITE (v. Vol. VII, 2c).

**MIGRATION, IONIC.**—Faraday's Laws of Electrolysis state that when an electric current is passed through a solution of an electrolyte, the mass of substance liberated at an electrode is proportional to the quantity of electricity passed and to the chemical equivalent of the substance. This indicates that such solutions contain ions which carry integral numbers of positive or negative charges; when a potential difference is applied they move towards the electrode of opposite charge and (in most cases) are discharged on arriving at the electrode surface. The discharged ions then appear as the products of electrolysis, or undergo secondary chemical reactions.

The fact that ions migrate can be demonstrated by analysing the solution before and after electrolysis. It is found that the concentration in the bulk of the solution remains constant, but near the electrodes it changes in a manner which can only be explained by assuming that all the ions within the potential field have moved towards the oppositely charged electrode. This principle is the basis of Hittorf's method of studying ionic migration (*see below*).

The *mobility* of an ion is its velocity of migration (in cm. per sec.) when it is situated in a field of unit potential gradient (1 v. per cm.). The velocity is directly proportional to the applied potential gradient, except at very high potentials (the "Wien effect") or in alternating fields of very high frequency (the "Debye-Falkenhagen effect") (v. **MOLECULAR CONDUCTIVITY**, this Vol., p. 160a).

Ionic mobilities are not definite constants for individual ions, but depend on temperature, the nature and viscosity of solvent, concentration, and the presence of other ions in the solution. The mobilities of the ions in a solution determine its equivalent or molecular conductivity (*q.v.*). According to Kohlrausch's Law of Independent Migration of Ions the total conductivity  $\Lambda$  of a

solution is the sum of the separate ion conductivities ( $l_+$  and  $l_-$ )

$$A = l_+ + l_- \quad (1)$$

The ion conductivities are related to the actual velocities of the ions ( $v_+$  and  $v_-$ ) by the factor  $F$  (the Faraday, 96,500 coulombs per gram-equivalent)

$$l_+ = Fv_+ \text{ and } l_- = Fv_- \quad (2)$$

These relations are true at all concentrations if the electrolyte is completely dissociated, but  $A$ ,  $v$ , and  $l$  remain functions of concentration. In extremely dilute solutions, however, the ions do become truly independent, and consequently  $v$  and  $l$  at infinite dilution can be regarded as constants for each ion. The mobility of the chloride ion is the same at infinite dilution in hydrochloric acid and in potassium chloride solution, but not in solutions of appreciable concentration owing to inter-ionic effects. Similarly, values of  $A_0$ , the limiting equivalent conductivity at infinite dilution can be computed from (1) if the limiting ion conductivities at infinite dilution are known. Table I gives some values of limiting ion conductances, and of corresponding mobilities calculated from them by (2). To calculate  $A_0$  for any salt add  $l_+$  and  $l_-$ ; e.g.,  $A_0$  for potassium nitrate— $l_{K^+} + l_{NO_3^-} = 63.65 + 62.6 = 126.2$ .

If the ions from a uni-univalent salt had equal mobilities and were present in solution in equal numbers they would carry the same amount of current during electrolysis. In general, however, anion and cation migrate at different rates, and therefore the faster-moving ion carries the greater share of the current. (In certain solids all the current is carried by the movement of one ion only.) The fraction of current carried by a given ion is called the transport number ( $T$ ) of the ion. For a uni-univalent electrolyte the transport number ( $T_+$ ) of the cation is  $T_+ = v_+ / (v_+ + v_-)$ ; that of the anion is  $T_- = v_- / (v_+ + v_-)$ , and obviously  $T_+ + T_- = 1$ .

The above considerations suggest three possible methods of studying the speed of migration of ions, namely;

(i) by direct measurement of the velocity in a known potential gradient;

(ii) by measuring the transport number and equivalent conductivity of the same (very dilute) solution: since, if the salt is completely dissociated,  $A = l_+ + l_- = F(v_+ + v_-)$  and  $T_+ = v_+ / (v_+ + v_-)$  it follows that  $v_+ = T_+(A/F)$  and  $v_- = T_-(A/F)$ . The usual practice is to extrapolate both  $A$  and  $T$  to infinite dilution and obtain limiting ion conductivities. MacInnes, Shedlovsky, and Longworth (J. Amer. Chem. Soc. 1932, 54, 2758) extrapolated the apparent values of  $l$  itself, using theoretical formulae which implicitly assume complete dissociation;

(iii) by assuming the  $l$  value of one ion [from measurements on other substances by method (ii)] that of the other ion can be found from either  $A_0$  or  $T_0$  alone. The usual starting point is potassium chloride; at 25°  $A_0 = 149.82$  and  $T_0 = 0.5094$ ; hence  $l_-$  at infinite dilution = 76.32 (MacInnes, Shedlovsky, and Longworth, *l.c.*).

In addition, transport numbers can be ob-

tained from e.m.f. measurements with cells containing liquid junctions (v. LIQUID JUNCTION POTENTIAL, Vol. VII, 355b).

### Experimental Determination of Ion Mobilities.

1. *The Moving-boundary Method.*—The rate of movement of a sharp boundary at the junction of two solutions is followed by any suitable means, such as an indicator colour change or difference of refractive index. The solutions must have one ion in common, the boundary must move towards the solution containing the faster non-common ion, and the lower solution must be the denser in order to avoid mixing. An example of the method is the determination of the velocity of the hydrogen ion by following the movement of a boundary separating hydrochloric acid below from dilute lithium chloride solution above, the boundary being made visible by a trace of Methyl Orange indicator. True ion mobilities can be obtained directly (but not with high accuracy) by this method if the potential gradient can be calculated from a knowledge of the dimensions of the apparatus and the conductivities of the solutions. More often, however, these are not known, but by measuring the volume ( $V$ ) through which the boundary sweeps in time  $t$  and also the quantity of electricity ( $Q$ ) passed, the transport number can be calculated. The relation is

$$T = FC(dV/dQ),$$

where  $C$  is the concentration of ion in gram-equivalents per c.c., and  $dV$  is the volume in c.c. swept through by the boundary during the passage of current  $dQ$  coulombs.

A small correction is required to allow for the change of volume which occurs at the electrode at the closed end of the apparatus. For example, if a silver-silver chloride cathode is used, the electrode reaction occurring is the reduction of silver chloride by hydrogen ions, and the metallic silver produced occupies a slightly different volume from the original silver chloride. For further details of the moving boundary method, see MacInnes and Longworth, Chem. Rev. 1932, 11, 171; D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.

2. *Hittorf's Method* (v. Vol. VI, 237d).—The principle of this method has been indicated above. Although simple and generally applicable, the determination depends on measuring a difference of concentration, and according to MacInnes and Longworth (*l.c.*) the accuracy obtained is not as high as in the best moving-boundary determinations. The agreement between the two methods is, however, excellent. In Hittorf's method the transport number of the cation is equal to the ratio of the number of gram-equivalents of solute which pass out of the anode compartment (or into the cathode compartment) to the total number of Faradays of electricity passed through the apparatus. In some cases there is an increase, in others a decrease of concentration in the neighbourhood of an electrode, depending on the cell used. For example, at a silver anode in silver nitrate solution, the observed change of concentration

is the balance of an increase of  $Q/F$  gram-equivalents by solution of the electrode and a decrease of  $(T_+)(Q/F)$  due to migration of silver ions towards the cathode. Since  $T$  is less than unity there is in this case a net increase of silver content.

Results obtained by Hittorf's method are complicated by the simultaneous transport of solvent, which is carried as solvation shells surrounding the ions (*see below*).

### Experimental Results.

**Ion Conductivities.**—Some typical data for equivalent ion-conductivities at infinite dilution ( $l$ ) are given in Table I, together with their temperature coefficients and derived mobilities.

TABLE I.—LIMITING EQUIVALENT CONDUCTIVITIES, TEMPERATURE COEFFICIENTS, AND ION MOBILITIES OF SOME COMMON CATIONS AND ANIONS IN AQUEOUS SOLUTION AT 18°C.

Ion.	Limiting conductivity ( $l$ ).	Temperature coefficient $\alpha = (1/l)(dl/dt)$	Mobility $v = l/F$ cm. per sec. per v. per cm.
H <sup>+</sup> (H <sub>2</sub> O).	315	0.0154	$32.7 \times 10^{-4}$
Li <sup>+</sup> . .	32.55	0.0265	3.37 "
Na <sup>+</sup> . .	42.6	0.0244	4.41 "
K <sup>+</sup> . .	63.65	0.0217	6.60 "
Ag <sup>+</sup> . .	53.25	0.0229	5.52 "
$\frac{1}{2}$ Ca <sup>++</sup> . .	50.4	0.0247	5.22 "
$\frac{1}{2}$ Ba <sup>++</sup> . .	54.35	0.0239	5.63 "
$\frac{1}{2}$ Cu <sup>++</sup> . .	45.3	—	4.70 "
OH <sup>-</sup> . .	174	0.0180	$18.0 \times 10^{-4}$
Cl <sup>-</sup> . .	66.3	0.0216	6.87 "
Br <sup>-</sup> . .	68.25	0.0215	7.07 "
I <sup>-</sup> . .	66.85	0.0213	6.93 "
NO <sub>3</sub> <sup>-</sup> . .	62.6	0.0205	6.48 "
$\frac{1}{2}$ SO <sub>4</sub> <sup>-</sup> . .	68.7	0.0227	7.12 "
$\frac{1}{2}$ CO <sub>3</sub> <sup>-</sup> . .	60.5	—	6.27 "
CH <sub>3</sub> COO <sup>-</sup>	35.0	0.0238	3.6 "

The high mobilities of hydrogen and hydroxyl ions are notable. Small ions of low atomic weight would be expected to move faster than larger ones carrying the same charge, since the viscous resistance should be less, but this is often not the case. For example, Table I shows that the mobilities of the alkali-metal ions are in the reverse order, viz.  $K > Na > Li$ . This is ascribed to a large "hydration shell" around the smaller ions owing to the more intense electrostatic field (*see "Solvation of Ions," below*).

The temperature coefficient of  $l$  is given as  $(1/l)(dl/dt)$ , i.e., the fractional increase of mobility per unit rise of temperature. It is seen to be approximately the same for all the ions except hydrogen and hydroxyl, namely, 0.026–0.021. This result is in agreement with the concept of ions behaving as spheres moving through a viscous fluid; the resistance according to Stokes's Law should then be proportional to  $\eta v$ , where  $\eta$  is the viscosity. Under constant applied potential the mobility,  $v$ , should be inversely proportional to the viscosity of the

solvent, i.e.,  $\eta v = \text{const.}$  Hence,  $(1/v)(dv/dt) = -(1/\eta)(d\eta/dt)$ . The viscosity of water at 18° is 1.056 centipoises and the temperature coefficient is  $-0.0265$ , whence  $-(1/\eta)(d\eta/dt) = 0.0254$ , which is of the same order as the temperature-dependence of mobility in Table I.

The relation  $\eta_0 v_0$  (or  $l_0 \eta_0$ ) = constant is known as Walden's Rule. It accounts fairly well for the change of  $l$  for a given ion in one particular solvent at different temperatures; e.g.,  $l_0 \eta_0$  for the acetate ion in aqueous solution is 0.367 at 0°, 0.363 at 50°, and 0.366 at 100°. Walden's Rule holds only very approximately for an ion in different solvents, probably because the degree of solvation varies with the solvent.

**Transport Numbers.**—Transport numbers of many salts have been measured by Hittorf's method; the results are mostly approximate and depend on the temperature and concentration used. For numerical data, *see* Landolt-Börnstein, "Physikal-Chemische Tabellen." The early work has been reviewed by Noyes and Falk (J. Amer. Chem. Soc. 1911, 33, 1436). Accurate measurements by Hittorf's method have been made in recent years by Jones and Dole (*ibid.* 1929, 51, 1073) and Jones and Bradshaw (*ibid.* 1932, 54, 138). Some very accurate determinations of transport number have been made by American workers by the moving-boundary method; some of their results are given in Table II.

TABLE II.—CATION TRANSPORT NUMBERS OF SOME SALTS IN 0.01N. AND 0.1N. AQUEOUS SOLUTIONS AT 25°C.

(D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.)

Electrolyte.	Cation Transport Number	
	0.01N.	0.1N.
HCl . . . . .	0.8251	0.8314
LiCl . . . . .	0.3289	0.3168
KCl . . . . .	0.4902	0.4898
KBr . . . . .	0.4833	0.4833
KNO <sub>3</sub> . . . . .	0.5084	0.5103
AgNO <sub>3</sub> . . . . .	0.4648	0.4682
CH <sub>3</sub> COONa . . . . .	0.5537	0.5594
CaCl <sub>2</sub> . . . . .	0.4264	0.4060
K <sub>2</sub> SO <sub>4</sub> . . . . .	0.4829	0.4890
H <sub>2</sub> SO <sub>4</sub> . . . . .	—	0.8145
K <sub>3</sub> Fe(CN) <sub>6</sub> . . . . .	0.4315	0.4410
Co(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub> . . . . .	0.5673	—

Owing to the high mobility of the hydrogen ion it carries more than 80% of the current during the electrolysis of an acid such as hydrochloric acid.

The fact that transport numbers are somewhat dependent on concentration shows that ion mobilities also vary (and unequally) with concentration. Consequently, the conductance ratio,  $A/A_0$  cannot be an accurate measure of the degree of dissociation, as was supposed by the early workers. The changes in conductivity due to ionic interaction can be calculated ap-

proximately for very dilute solutions by the Debye-Hückel-Onsager theories (v. MOLECULAR CONDUCTIVITY, this Vol., p. 160a). Interpolation formulæ have been proposed by Jones and Dale (l.c.) and by Longworth (*ibid.* 1932, 54, 2741), who used an empirical equation with two adjustable constants to represent the change of  $T$  with concentration up to 0.1N.

**Solvation of Ions** (v. Vol. VI, 295c).—The amount of solvent permanently bound to ions in solution has been investigated by studying the transport of solvent during electrolysis (Washburn, *ibid.* 1909, 31, 322; Washburn and Millard, *ibid.* 1915, 37, 694; Reny and Reiser, Z. physikal. Chem. 1926, 124, 394). In one method a non-electrolyte such as urea or sucrose is added to the solution to act as a reference substance to indicate movement of solvent; another employs a semi-permeable membrane. Recent work on this problem is discussed by Hepburn (Phil. Mag. 1938, [vii], 25, 1074). At the present time it is possible to determine differences in the degree of solvation of anion and cation, but the absolute values cannot be obtained. The hydrogen ion is believed never to occur as a free proton in solution, but is always attached to one or more solvent molecules. If it exists in water as  $H_3O^+$ , then the chloride ion carries about 4, lithium 14, sodium 8, and potassium 5 molecules of water of hydration. In some cases there may be definite co-ordination of water to an ion, but it is more probable that the molecules of solvation are clustered statistically round the ion by dipole orientation in the electrostatic field.

**Abnormal Transport Numbers**.—In certain cases the transport number varies greatly with concentration and may even appear to become greater than unity. This generally indicates the formation of complex ions, and, in fact, the method can be applied in some instances to determination of the structure of complexes. Hittorf showed by measurements of electrolytic transport that potassium silver cyanide solutions contain the  $[Ag(CN)_2]^+$  ion.

Hartley and his co-workers (Trans. Faraday Soc. 1936, 32, 795; 1938, 34, 1283, 1288) have used a combination of conductivity and transport measurements (the latter by a special modification of the moving-boundary method) to study "micelle" formation in solutions of colloidal electrolytes. "Transport numbers" as high as 3.3 were found with solutions of cetyl pyridinium iodide.

J. A. K.

MILCH DEN (v. Vol. V, 72c).

**MILDEW- AND ROT-PROOFING OF TEXTILES**.—Mildewing of textiles, which is caused by the growth of micro-organisms, is manifested initially by the development of a musty odour and the appearance of variously coloured stains, and later by more serious deterioration resulting in loss of tensile strength. The two effects, staining and decay, have often been separated, and the former only referred to as mildewing, but recent investigations indicate that such a division is artificial. Under appropriate conditions wool and related animal fibres, cotton, silk, bast fibres, and most rayons, whether in the form of fibres, yarn or cloth, are

liable to attack. Most of the research has, however, been carried out on the degradation of cotton and wool, although the War of 1939-45 has stimulated activity in the rot-proofing of jute.

#### COTTON.

Micro-organisms responsible for the mildewing of cotton are mainly the lower fungi, bacteria, and possibly *Actinomyces*. Species of fungi most commonly met with are *Aspergillus*, *Penicillium*, *Fusarium*, *Alternaria*, *Metarizium*, *Chaetomium Globosum*, and *Rhizopus*, whilst *Cladosporium*, *Botrytis*, *Acrothecium*, *Stysanus*, and others have been isolated in a few instances (Bright, Morris, and Summers, J. Text. Inst. 1924, 15, r547; Galloway, *ibid.* 1930, 21, r277; A. C. Thaysen and H. J. Bunker, "Microbiology of Cellulose, Hemicellulose, Pectins, and Gums," Oxford, 1927, p. 254; Goodavage, Amer. Dyestuff Rep. 1944, 33, r265). The vulnerability of all forms of cotton, ranging from raw fibres to finished cloth, has led to the view that with certain fungi the primary cause of infection may be in the raw cotton itself. Any initial contamination of this type would persist through the operations of ginning, baling, and spinning, and although it would be destroyed during bleaching or mercerising, the material after such chemical treatment would still be liable to infection by fungal spores in the atmosphere.

Favourable conditions are necessary for the development of mould fungi, and temperature, relative humidity, and adequate food supply are important. The requirements of the various fungi differ considerably. For example, the optimum temperature for a white *Aspergillus* was shown to be 37°C., whereas that for a green *Penicillium* is 27°C. (Bright, Morris, and Summers, l.c.). Most species grow very slowly at temperatures less than 7°C., but the normal temperatures prevailing during the storage and processing of cotton are suitable for their development. It is claimed that fungi are killed by lack of water, but actually the spores merely become dormant and, even after several months, will grow whenever the necessary water is available. From the results of various investigations (J. D. Galloway and R. Burgess, "Applied Mycology and Bacteriology," London, 1937, p. 131) it appears that for successful mould-growth, cotton should have a regain of at least 8-9%, i.e., it should be in equilibrium with an atmosphere of more than 75% relative humidity. The precise minimum relative humidity required depends on the particular fungus, e.g., *Rhizopus*, 90%, *A. candidus*, 75%, and *A. niger*, 95% (Galloway, J. Text. Inst. 1935, 26, r123). As all fungi can feed on sugars, proteins, and starches, the last being degraded into sugars which are adsorbed directly, their wants are supplied not only by the cellulose fibres, but also by starches and sizes present in cotton yarn and cloth (Morris, *ibid.* 1926, 17, r1, r23; 1927, 18, r99). Fungi which are incapable of destroying cellulose are often present on mildewed goods and must feed on starches and sizes, or on degradation products of cellulose liberated by other fungi. The several

types of cotton show different degrees of susceptibility to degradation, American cotton being the most resistant, but all are rendered much more susceptible by the presence of sizes, especially those containing starches and flour.

The nutritional conditions outlined above also favour the development of bacteria, but these organisms require more moisture, and in general cause degradation only when the cotton is wet (A. C. Thaysen and H. J. Bunker, Second Report of the Fabrics Research Co-ordinating Committee, H.M. Stationery Office, 1930).

Very early stages of mildew may be detected by staining with picronigrosine (Bright, J. Roy. Microscop. Soc. 1925, 271, 141), which renders the mycelium visible, or with Cotton Blue in lactophenol (Nopitsch, Textilber. 1933, 14, 139), which stains spores blue, whilst the Congo Red test, based on the appearance of cotton hairs swollen in strongly alkaline solution and subsequently stained with Congo Red, is also of considerable value in detecting microbiological attack (Bright, J. Text. Inst. 1926, 17, T396; Clegg, *ibid.* 1940, 31, T49). To estimate quantitatively the extent of decay, loss of tensile strength is often employed, but Thaysen and Fleming (Biochem. J. 1920, 14, 25) have developed a test in which 0.2 g. of a sample is mixed with 10 ml. each of a 15% sodium hydroxide solution and carbon disulphide, and allowed to soak until the maximum degree of swelling is attained. If the cuticle is substantially damaged the characteristic "beading" produced on normal cotton disappears, and by means of a suitable technique the extent of degradation can be estimated.

**Prevention of Mildew.**—Mildew of cotton may be prevented by maintaining a temperature which is too low, and a supply of moisture which is insufficient for the growth of fungi. This course is possible in storage rooms, but is clearly not of universal application. When storage under ideal conditions is not practical, the material is treated with chemicals, popularly known as "antiseptics," which inhibit the growth of micro-organisms on the fibres and on their accompanying sizes, and are applied either as a dressing to the material, or incorporated into the size mixing. According to Fargher, Galloway, and Probert (J. Text. Inst. 1930, 21, T245), an ideal antiseptic for general use in the cotton industry should have the following properties, in addition to a high antiseptic efficiency:

- (i) It must not volatilise during the boiling of the size mixing or finishing paste, or the drying of the sized yarn or filled cloth.
- (ii) It must be unaffected by heat, by metallic surfaces with which it may come into contact, and by any of the ingredients commonly used in finishing pastes.
- (iii) It must be sufficiently soluble to ensure uniform distribution throughout the mixing.
- (iv) It must have no appreciable colour or odour, and must not develop any colour in slightly acid or alkaline solutions. This particular requirement,

however, is not absolutely necessary provided that the colour is not objectionable, e.g., cotton proofed with mineral khaki.

- (v) It must have no adverse effects on the cotton.
- (vi) If used in a cloth that is to be dyed and finished subsequently, it must not affect the results produced by these processes.
- (vii) To be generally useful, the cost, for equal protection, should not exceed that of zinc chloride.

The toxicity of the reagent should, of course, be high, and it is considered by Goodavage (*l.c.*) that for complete protection against mildew the proofing compound should inhibit the growth of *Chaetomium globosum*, *Metarrizium*, *Aspergillus*, and *Penicillium*.

Of the very numerous compounds suggested, some have been used in technical investigations, and data concerning their effectiveness are available, but others are the substance of patent specifications and there is little scientific information regarding their utility. The more common reagents are described below, but it should be pointed out that many are more lethal to certain fungi than to others, and that although many do not conform to the requirements of an ideal antiseptic, this does not prevent them from being useful for certain purposes, e.g., coloured compounds may be used when proofing mechanical fabrics. The effectiveness of many of the compounds is often increased by the subsequent application of a water-proofing agent, which may be of the wax-emulsion type or an aluminium salt.

**Zinc Chloride.**—At least 0.8% of this compound on the total weight of cotton is necessary. If the cloth or yarn is subjected to high temperatures, difficulties are encountered because of the decomposition of zinc chloride to yield hydrochloric acid, which causes tendering. Morris (*l.c.*, 1927) has shown that in a size, 8–10% of zinc chloride (calculated as a percentage of the total starch) must be used with wheaten flour, and 6% in the case of other starches. Zinc chloride appears to be a good antiseptic for use on heavily sized goods, but may cause trouble by forming zinc soaps by interaction with softening agents.

**Chromium Compounds.**—These are usually employed in the form of a pigment referred to as "mineral khaki." The oldest method consists in impregnating cotton with salts of chromium and iron (usually ferric sulphate or ferric alum and chrome alum), and fixing the adsorbed salts by development with sodium hydroxide or carbonate. This leaves the cloth alkaline, and hence a process has been devised in which the development is done by potassium chromate. Recent work by Race, Rowe, and Speakman (J. Soc. Dyers and Col. 1941, 57, 213; 1942, 58, 32, 61) has shown that the pigments produced in the two cases differ. The second method results in the production of a chromium chromate of the formula  $3\text{Cr}_2\text{O}_3 \cdot 4\text{CrO}_3$  and an iron chromate  $3\text{Fe}_2\text{O}_3 \cdot 2\text{CrO}_3$ . During washing which follows the treatment, the

chromates are hydrolysed to form hydrated ferric and chromic oxides, but the chromic oxide so produced differs from that deposited on the fibres by development with caustic soda or sodium carbonate, the former containing more alkali-soluble chromium and being more deeply coloured. Since the more expensive chromate process provides superior protection against moulds, and also leaves the cotton approximately neutral, it was considered desirable to imitate it by modifying the technique of alkali development, and the use of ammonia at 80°C. was advocated. The pigment deposited by this method contains appreciable amounts of alkali-soluble chromium, and closely resembles that produced by the chromate process, whilst at the same time the cotton is not rendered strongly alkaline. Jarrell, Stuart, and Holman (Amer. Dyestuff Rep. 1937, 26, 495) believe that the degree of protection produced by most "mineral khaki" dyeings is inadequate, but have shown that if copper salts are also present to the extent of at least 0.11% (calculated on the weight of cotton), satisfactory protection is given.

**Copper Salts.**—These have considerable toxic power and have been employed for mildew-proofing, although their use is somewhat limited as they stain the material green, and in certain forms are comparatively expensive. Cuprammonium hydroxide (used in the manufacture of Willesden fabrics), copper sulphate applied with caustic soda, basic copper carbonate formed by the interaction of copper sulphate and soda ash, copper soaps, copper naphthenates (often applied along with other naphthenates) and copper propionyl acetate have been shown to be effective.

**Organic Compounds.**—Many organic compounds have been suggested for mildew-proofing, and the following are illustrative of the wide range: organo-metallic compounds of mercury, such as mercury *p*-tolyl salicylate, *p*-acetoxy-mercuriacetanilide (Fargher, Galloway, and Probert, *l.c.*), and phenyl mercury oleate (Furry, Robinson, and Humfeld, Ind Eng. Chem. 1941, 33, 538); alkylated dimethylbenzylammonium phosphate, followed by a methyl acrylate resin; substituted phenols, of which the most important are *o*-phenylphenol, and 2-chloro-*o*-phenylphenol; 2:2'-dihydroxy-5:5'-dichlorodiphenylmethane; tribromo- and trichloro-phenol, and pentachlorophenol; and salicylanilide ("Shirlan," I.C.I., Ltd.).

#### RAYON.

Acetate rayon is resistant to mildew and the treatment of cotton or cellulose rayons with acetic acid, acetic anhydride, and acetyl chloride, which presumably function by acetylating the cellulose, yield a cellulose acetate which is resistant to mould attack.

#### WOOL.

The growth of micro-organisms on wool, as on cotton, is determined by food, temperature, and moisture, the last being most important. In atmospheres of about 90% relative humidity, moulds, especially those of the genera *Penicillium* and *Aspergillus*, will flourish, but in damper

atmospheres and when wool is immersed in water, bacteria such as *B. mesentericus*, *B. subtilis*, and *B. mycoides*, and certain *Actinomyces*, attack the fibre (Burgess, J. Text. Inst. 1924, 15, T573) and result in degradation to cortical cells. The condition and type of wool determine its susceptibility to attack, the presence of natural grease and suint, added soaps and oils, and products of alkaline hydrolysis increasing the ease with which it is damaged (Burgess, J. Soc. Dyers and Col., 1931, 47, 96). Similarly, the pH of the fibres is important, an alkaline state favouring the development of bacteria and hindering fungoid growth, whereas increasing acidity functions in the opposite manner. Staining accompanies the growth of both moulds and bacteria.

Microbiological damage can frequently be minimised by storage under suitable conditions, but where this is not possible, use has to be made of antiseptics, a number of which have been examined by Burgess (J. Text. Inst. 1934, 25, T289, 391). This author, however, seldom employed cultures of bacteria, but as a result of an examination which showed the action of trypsin to be similar to that of proteolytic bacteria, preferred to test the efficiency of antiseptics by measuring their inhibiting action on the degradation of wool by a buffered solution of trypsin. He has demonstrated that for practical purposes satisfactory protection is given by the use of 0.4% of sodium fluoride, 0.7% of "Shirlan N.A.", 0.67% of sodium *o*-phenylphenate, or 1% of sodium silicofluoride, whilst phenol, formalin, benzoic acid, mercuric chloride, salicylic acid, zinc silicofluoride, and thallium carbonate also have considerable antiseptic power. Treatment of wool with potassium dichromate confers some degree of resistance to attack by micro-organisms, and this effect is considerably enhanced if "Eulan N" is applied at the same time. Copper salts, especially the naphthenates, are also good antiseptics, but their use is limited on account of staining. These compounds are very effective when applied along with eutal, although the latter has very little preservative action when used alone.

#### BAST FIBRES.

The microbiological degradation of flax and hemp is of especial importance in connection with their use in the manufacture of fishing and similar nets, and in retting of flax to produce the commercial fibre. The latter is discussed in Vol. V, 159c, and it remains only to mention methods of preservation. Treatments with rubber latex (Olie, through Second Report of Fabrics Research Co-ordinating Committee, H.M. Stationery Office, 1930) after impregnation with eutal and other fungicides, and treatments with copper oleate and tar (Taylor and Wells, Bureau of Fisheries Documents, Nos. 947 and 998, Washington), or copper naphthenate are considered to give satisfactory results. The fungicide should not be leached out during the life of the textile.

Although jute is heavily lignified it is very susceptible to mildew and decay, a fact which has considerable commercial significance on



account of the use of jute for sandbags and similar articles. Degradation is slight under dry conditions, but in the presence of water, attack by moulds, bacteria, and *actinomyces* is rapid. As jute is cheap, any acceptable proofing operation must also be cheap, and hence many treatments which are suitable for cotton are impracticable for jute. The most recent results (Armstrong, Chem. and Ind. 1941, 60, 668) on the preservation of sandbags indicate that tar distillates having a tar-acid content between 5 and 10%, copper salts of oleic, stearic, and naphthenic acids, copper chromate, colloidal copper, basic copper carbonate, and cuprammonium compounds, when used under optimum conditions, are effective. In order to attain satisfactory microbiological resistance, at least 0.35% of metallic copper on the weight of the fibre must be deposited, but in practice not less than 0.8% should be applied initially. When proofing with cuprammonium salts a copper content of 1.0–1.5% is desirable, whilst at least 25% of creosote is necessary, although this may be reduced to 20% if 0.5% of copper is also deposited on the fibre. In addition to rotting due to exposure in water, degradation of jute may also take place in the centre of bales, a phenomenon which is known as "heart damage" (Cross and Bevan, J.S.C.I. 1908, 27, 1129; Finlow, Mem. Dep. Agric. India, 1918, 5, 33; Thaysen and Bunker, "Microbiology of Cellulose, Hemicellulose, Pectins and Gums," London, 1927, pp. 258–260).

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Mildew-proofed cotton fabrics, Goodavage, Amer. Dyestuff Rep. 1943, 33, p265.  
Finishing of Army ducks, Bertolet, *ibid.*, p. p214.

C. S. W.

#### MILFOIL (v. Vol. I, 119d). MILK.

##### 1. GENERAL DESCRIPTION OF MILK, INCLUDING COLOSTRUM.

The composition of the thick secretion (colostrum or beestings) of the mammary gland is especially designed for the suckling of the newly born offspring with its limited digestive powers. With the development of the offspring the composition of the colostrum secreted gradually changes and assumes the composition of the milk appropriate to the particular species of mammal. The secretion of this milk continues during the lactation period and subsequently diminishes and largely ceases. The term "milk" is confined to the lacteal secretion of the milch cow unless otherwise stated.

Both the colostrum and the milk which follows consist essentially of an emulsion of butterfat in a continuous aqueous phase in which are lactose and a colloidal suspension of casein, stabilised mostly by albumin and globulin. Inorganic salts, some in solution and some in

colloidal association with the casein, *e.g.*, calcium and magnesium phosphates, are also present, together with citrates and other minor constituents, some of which (*e.g.*, the vitamins), are of major importance.

The percentage composition of the colostrum of the cow secreted during the first week after parturition is given in Table I. Typical figures for cows' milk are also included for comparison.

TABLE I.—COLOSTRUM (OR BEESTINGS).

(Engel and Schlag, Milch. Forsch. 1924, 2, 1.)

Time (days after calving).	0	1	2	4	7	Milk (see Table II).
Water .	73.01	87.23	88.56	88.15	87.87	87.25
Fat . .	5.10	3.40	2.80	2.80	3.45	3.75
Casein .	5.08	2.76	2.63	2.68	2.42	2.63
Lactalbumin,						
Lactoglobulin and	11.34	1.48	0.99	0.82	0.69	0.55
Proteose-Peptide						
Lactose .	2.19	3.98	3.97	4.72	4.96	4.70
Ash . .	1.01	0.86	0.83	0.83	0.84	0.75
Cl as NaCl	0.153	0.156	0.149	0.135	0.113	0.105
Sp.gr. .	1.067	1.034	1.032	1.034	1.032	1.032
F.P. depression, °C. .	0.605	0.575	0.580	0.555	0.570	0.550

[The pre-colostral fluid obtainable from the udder of cows prior to parturition is similar in composition to colostrum (Woodman and Hammond, J. Agric. Sci. 1923, 13, 180).]

During the period of secretion the percentages of lactalbumin, lactoglobulin (and proteose-peptide), casein, ash, and chloride of the colostrum decrease, while the lactose content increases. A particular characteristic of colostrum during the first 2–3 days of secretion is the heat coagulability due to its high content of lactoglobulin (Crowther and Raistrick, Biochem. J. 1916, 10, 434), which is believed to be derived unchanged from the blood-stream (*idem, ibid.*; Wells and Osborne, J. Infect. Dis. 1921, 29, 200; Amer. Chem. Abstr. 1921, 15, 3677). Its iron content is also high, being approximately seventeen times that of milk (Fleishman, "The Book of the Dairy," London, 1896, p. 36).

Definition.—In Britain there is no official definition of milk. According to the Sale of Milk Regulations, 1939, and for the purpose of the Food and Drugs (Adulteration) Act, 1928, milk containing less than 3% of fat or less than 8.5% of non-fatty solids is presumed not to be genuine unless the contrary is proved to be the case.

Incidentally, according to the Public Health (Condensed Milk) Regulations, 1923, milk contains 12.4% of milk solids, including 3.6% of fat (both minimum values). This presumably is intended to indicate the composition of "average" milk, as distinct from the lower limits for genuine milk.

The Federal definition of the U.S.A. is: "Milk is the fresh, clean lacteal secretion obtained by the complete milking of one or more

healthy cows, properly fed and kept, excluding that obtained within 15 days before and 10 days after calving, containing not less than 8.5% of solids-not-fat, and not less than 3.25% of milk fat."

The Geneva Congress defined milk as "The integral product of entire and uninterrupted milking of the female milch cow in good health and well nourished and not over worked. It ought to be collected in the proper manner and contain no colostrum."

## 2. AVERAGE COMPOSITION OF MILK.

Numerous factors (considered later) affect the composition of cow's milk, which is by no means constant, but the variations in composition are less evident in bulked herd-milk. The average percentage proportions of the major constituents of milk are given in Table II.

TABLE II.

Reference No.	1	2	3	4	5
Fat . . .	3.61	3.75	3.67		
Non-fatty solids . .	8.77	9.00	9.02		
Total N . .				0.5246 (100)	0.5244 (100)
Total protein*		3.20	3.42	3.18 (95)	3.15 (94.3)
Casein *			2.86	2.63 (78.5)	2.61 (78.1)
Lactalbumin *				0.31 (9.2)	0.34 (10.0)
Lactoglobulin *				0.11 (3.3)	0.10 (3.1)
Proteose-peptone *			0.50	0.13 (4.0)	0.10 (3.1)
Non-protein N		(0.03)		0.0263 (5.0)	0.0267 (5.7)
Non-protein bodies .		0.20			
Lactose . .		4.70	4.78		
Ash . . .		0.75	0.73		
Other bodies .		0.15	0.20		

\* Calc. as N×6.38.

The figures in parentheses represent nitrogen contents calculated as the percentage of total nitrogen in the milk.

<sup>1</sup> Average of 771,662 samples, H. D. Richmond, "Diary Chemistry," 4th ed. revised by G. D. Elsdon and G. H. Walker, London 1942, p. 7

<sup>2</sup> Composition of milk usually quoted, *op. cit.*, p. 2.

<sup>3</sup> Average of results of various observers, W. L. Davies, "Chemistry of Milk," London, 1939, p. 19.

<sup>4</sup> Based on analyses of bulk milk of mixed herds (England) (Rowland, J. Dairy Res. 1938, 9, 47).

<sup>5</sup> Calculated from reported analyses of mixed herds (U.S.A.) (Menefee, Overman, and Tracy, J. Dairy Sci. 1941, 24, 953).

The above results are subject to certain qualifications: those quoted from reference <sup>1</sup> represent approximately 45% of commercial samples and 55% of Public Analysts' samples, some of the latter probably being adulterated with water. These average figures must therefore be considered slightly low. The results from reference <sup>3</sup> are averages of the average results recorded by different observers, using in many cases different methods of analysis. While there is no serious criticism of most of the figures on that account, the individual protein contents

must be accepted with reserve, and the total protein figure may be high, as it is possible that in some cases it has been calculated from the total nitrogen content of the milk. The results from reference <sup>4</sup> give probably the most accurate detailed distribution of the protein bodies in milk. These results are confirmed by American workers (reference <sup>5</sup>) using essentially the same method of analysis. The best approximation to the average composition of milk is probably a combination of the results from references <sup>2</sup> and <sup>4</sup>. It should be remembered that the recorded figure for ash is slightly higher than the mineral content (*see* Section 3 (b) (v)) and the figure in reference <sup>2</sup> for "other bodies" (calculated by difference) is accordingly slightly low.

## 3. THE CONSTITUENTS OF MILK.

(a) The Disperse (Fatty) Phase.—*The fat globules of milk, surrounded by a surface layer containing protein and phosphatides and also, according to Kou et al. (Nature, 1944, 154, 82), carotenoids and cholesterol, are dispersed in the aqueous phase, forming an emulsion. The size distribution of these globules is affected by the breed, health, and individuality of the cow. It also varies according to the stage of the lactation period of the animals and with the type of food consumed, dry feeding producing smaller fat globules in the milk (Hunziker, Purdue Agric. Exp. Sta. Bull. No. 159, 1912). The effect of the stage of the lactation period is most conveniently illustrated by the size-frequency distribution graph (Fig. 1) constructed from the results of Van Dam and Sirks (Verslag. Onderz. Rijks. 1922, 26, 106). (In these curves the mid-points of each range of diameters of fat globules are plotted against the number of fat globules occurring in that range, expressed as a percentage of the total number of globules measured.) As lactation progresses an increase in the number of globules less than 2 $\mu$ . and a decrease in globules more than 4 $\mu$ . in diameter is evident (Lyons and O'Shea, Sci. Proc. Roy. Dublin Soc. 1934, 21, 123).*

## (b) The Continuous (Aqueous) Phase.

### (i) The Proteins of Milk.

For detailed properties, constituent amino-acids, etc., *see* under PROTEINS. In the present article the proteins are considered only from the point of view of their relationship to the characteristic properties of milk.

(a) Casein.—The terminological confusion concerning this protein has already been mentioned (*v. CASEIN*, Vol. II, 411a). The term "caseinogen" is applied to the protein as it exists in milk, and "casein" to the protein separated from milk by rennet, acid, etc. In the alternative terminology, chiefly adopted in the U.S.A., no such differentiation is made, "casein" being applied to the protein whether or not separated from milk, except in the special case of the rennet-precipitated protein which is termed "paracasein." Since casein has not been characterised as a chemical entity, the method for its determination and isolation (based on acid



precipitation at pH 4.7) serves to define it. Methods for its isolation and determination of its molecular weight by ultracentrifugal studies have already been described (Vol. II, 412*a*). It should, however, be pointed out that according to Svedberg (Nature, 1931, 128, 999) polymerisation and aggregation occur during its isolation, and consequently the recorded results do not apply to the protein "caseinogen" as it exists in milk (see also Section 4 (p. 103*b*), on "Physico-Chemical Relationship of Constituents").

(*b*) *Soluble Proteins*.—These are generally considered to consist of lactalbumin and lactoglobulin, which may be separated from fat-free milk in a variety of ways. The procedure of Crowther and Raistrick (Biochem. J. 1916, 10,

434) is based on the removal of casein by addition of potash alum, followed by saturation of the filtrate with magnesium sulphate to precipitate lactoglobulin, and then, after filtration, saturation of the solution at 40°C. with sodium sulphate to precipitate lactalbumin. Later Sjögren and Svedberg (J. Amer. Chem. Soc. 1930, 52, 3650) prepared crystalline lactalbumin by removal of casein and lactoglobulin by half-saturation with ammonium sulphate and precipitation of the lactalbumin from the filtrate by addition of acetic acid to pH 5.2. Palmer (J. Biol. Chem. 1934, 104, 359) prepared what he called "lactoglobulin" from casein-free whey by precipitation with sodium sulphate, but Pedersen (Biochem. J. 1936, 30, 961) considers

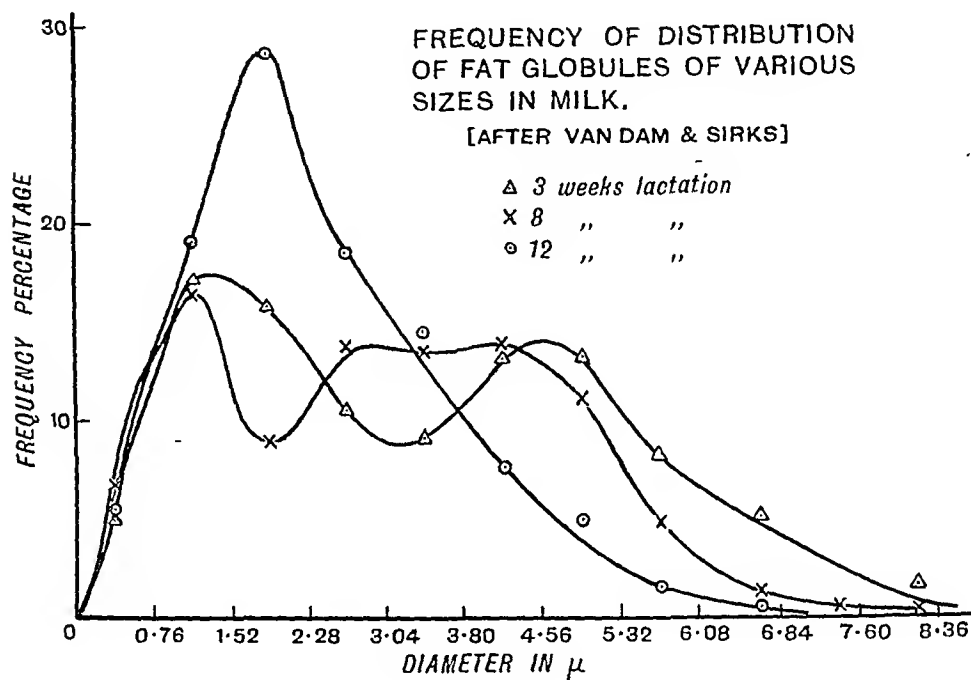


Fig. 1.

that this substance was probably part of the lactalbumin fraction. Incidentally, it may be mentioned that Crowther and Raistrick (*l.c.*) and also Howe (J. Biol. Chem. 1922, 52, 51) separated substances termed "euglobulin" and "pseudoglobulin" by fractional precipitation with sodium sulphate.

During these precipitations, including that of casein, the possibility must be borne in mind that changes in the proteins, especially molecular aggregation, may take place, and consequently the substances isolated are not necessarily identical with those present in the original milk. This criticism does not apply when fat-free milk is subjected to the Svedberg ultracentrifugal method used for studying the molecular sizes of proteins. By this method Pedersen (Biochem. J. 1936, 30, 948) and Kekwick (quoted by Pedersen) have indicated that in milk from which the large caseinogen particles have been removed by ultracentrifuging, there are three soluble

proteins: (i) a protein of low molecular weight (Kekwick); (ii) a globulin-like homogeneous protein of molecular weight 39,000, similar to that of Palmer (*l.c.*), having its isoelectric point at pH 5.19 in acetate buffer (these two proteins constitute what is normally termed "lactalbumin"); and (iii) the protein generally known as lactoglobulin.

Lactalbumin is soluble in water, with isoelectric point at pH 4.55 (according to Csonka *et al.*, J. Amer. Chem. Soc. 1926, 48, 763), or 5.2 (according to Sjögren and Svedberg, *l.c.*). It may be denatured and coagulated by surface-adsorption and by a variety of treatments, including exposure to light, pressure, and heat. The ultracentrifugal method in the hands of the last-named investigators, has indicated that "purified" lactalbumin has molecular weight varying from 12,000 to 25,000.

This protein exists in colostrum and, according to Woodman (Biochem. J. 1921, 15, 187),

whose conclusions are confirmed by serological studies of Sasaki (Arb. med. Univ. Okayama, 1930, 1, 550; J. Dairy Res. 1933-34, 5, 80), is not identical with blood-serum albumin.

*Lactoglobulin* is a heat-coagulable protein with acidic properties. Although its isoelectric point is reported to be pH 5.4 (that of blood-serum globulin), maximum heat-coagulation of lactoglobulin+lactalbumin is effected at pH 4.35-4.80. Lactoglobulin is insoluble in water, but soluble in dilute acids and mineral salt solutions. The lactoglobulin of milk and of colostrum are identical with blood-serum globulin, according to Howe (*l.c.*).

#### (ii) *The Minor Nitrogenous Constituents of Milk.*

These are generally understood to include all the nitrogenous bodies with the exception of the casein, lactalbumin, and lactoglobulin. They include traces of other proteins and phosphatides associated with the fat globules, together with secondary proteins of a proteose-peptone nature, and the residual nitrogenous bodies, namely, amino-acids, phosphatides, purine bases, urea, ammonia, etc.

The nature and quantity of the minor nitrogenous constituents depend upon the method of removing the casein, lactalbumin, and lactoglobulin. Heat treatment of milk (10 minutes at 100°C.), followed by adjustment of the pH to 4.7 at ca. 40°C., removes the above-mentioned proteins, and subsequent treatment with 8% trichloroacetic acid precipitates the *proteose-peptone* fraction, leaving in solution the *residual nitrogenous fraction* (Rowland, *ibid.* 1937, 8, 6). Alternatively, fat-free milk may be defeated with certain protein precipitants, leaving in the filtrate the last-named fraction, the quantity and composition of which depend to some extent on the precipitant used (Kieferle and Gloetzl, *Milch. Forsch.* 1931, 11, 62; Muehberg, *ibid.* 1933, 15, 50).

A detailed study of the precipitation of the proteins from milk by trichloroacetic acid has shown that concentration of the acid and temperature are of importance (Rowland, J. Dairy Res. 1938, 9, 30). At room temperature, maximum precipitation of the proteins (and hence minimum residual nitrogenous fraction) is obtained with a concentration of at least 8% (preferably 12%) of the acid, whereas at elevated temperature [*e.g.*, at 70°C. for 30 minutes with 4% of the acid, as in Moir's method (Analyst, 1931, 56, 228)] hydrolysis of protein (and so increased residual nitrogenous fraction) results.

As the residual nitrogenous constituents are largely dialysable, dialysis offers a further possible method for their separation from milk proteins.

Rowland (*l.c.*) found that the soluble protein fraction remaining after removal of casein (precipitation by 8% trichloroacetic acid at room temperature) was composed of approximately 24% of proteose-peptone fraction and 76% of lactalbumin and lactoglobulin.

The proportion of the various constituents of the residual nitrogenous fraction are shown in Table III.

TABLE III.—RESIDUAL NITROGENOUS FRACTION OF MILK.

	Mg. per 100 g.	N: mg. per 100 g.	Ref.
<i>Amino-acids and Amides.</i>			
Amino N . . .	2.9-14.7	2.0-14.7	1, 2, 3, 4, 5
Lysine, Arginine, Histidine . . .	present	present	6
Leucine . . .	0.2	0.08	7
Glycocoll . . .	65.2	12.7	7
Tyrosine . . .	0.0	0.70	7
Aspartic acid . . .	2.0	0.30	7
Glutamic acid . . .	5.4	0.66	7
Creatine . . .	5.3-11.8	1.7-3.8	1, 2, 3
Creatinine . . .	3.2-7.3	1.2-2.7	1, 2, 3
Urea . . .	22.3-47.1	7.1-15.0	1, 2, 3, 8
Hippuric acid . . .	present	present	21
<i>Phosphatides.</i>			
Lecithin . . .	present	present	9, 10, 11
Kephalin . . .	present	present	11, 12
<i>Purines.</i>			
Uric acid . . .	3.3-7.5	1.1-2.5	1, 2, 3, 8
Adenine . . .	0.50	0.26	6, 20
Guanine . . .	1.0	0.46	6, 20
Hypoxanthine . . .	present	present	6
Methylguanidine . . .	present	present	19
Nucleotides . . .	2.3		16
<i>Other bodies.</i>			
Ammonia . . .	0-2.1	0-1.7	1, 4, 8, 13, 14, 15
Thiocyanate (as CNS) . . .	0.013	0.22	15
Choline (as hydrochloride) . . .	40		17
Trimethylamine . . .	present	present	22
Trimethylamine oxide . . .	present	present	23
Orotic acid . . .	present	present	24
Vitamins containing N (see Table XII).			

<sup>1</sup> Kieferle and Gloetzl, *Milch. Forsch.* 1931, 11, 62.

<sup>2</sup> Bleyer and Knollman, *Biochem. Z.* 1924, 153, 450.

<sup>3</sup> Denis and Minot, *J. Biol. Chem.* 1919, 37, 353.

<sup>4</sup> Viale and Rabbeno, *Biochim. Terap. sperim.* 1921, 8, 325; *Amer. Chem. Abstr.* 1922, 16, 2354.

<sup>5</sup> Spirito, *Ped. riv.* 1920, 34, 921; *Amer. Chem. Abstr.* 1927, 21, 284.

<sup>6</sup> Hijkkn, *J. Biol. Chem.* 1922, 51, 165.

<sup>7</sup> Flehner and Vendell, *Bull. Soc. pharmacol.* 1921, 28, 360, 401.

<sup>8</sup> Muehberg, *Milch. Forsch.* 1933, 15, 50.

<sup>9</sup> Osborne and Wakeman, *J. Biol. Chem.* 1915, 21, 539.

<sup>10</sup> Arbenz, *Mitt. Lebensm. Hyg.* 1919, 10, 63.

<sup>11</sup> Schwarz and Mezler-Andelberg, *Biochem. Z.* 1928, 194, 362.

<sup>12</sup> Torrisi, *Boll. Soc. Ital. Biol. sperim.* 1934, 9, 1011.

<sup>13</sup> Burstein and Frum, *Z. Unters. Lebensm.* 1935, 69, 421.

<sup>14</sup> Kluge, *ibid.* 1936, 71, 232.

<sup>15</sup> Niemczycki and Gerhardt, *Lait*, 1936, 16, 1019.

<sup>16</sup> Bleyer and Knollman, *Biochem. Z.* 1924, 153, 450.

<sup>17</sup> Rhinn, *Bull. Wnsh. Agric. Exp. Stn.* 1911, No. 410, 33.

<sup>18</sup> Bleyer and Knollman, *Biochem. Z.* 1925, 155, 54.

<sup>19</sup> Mueller, *Z. Biol.* 1926, 84, 553.

<sup>20</sup> Voegtlin and Sherwin, *J. Biol. Chem.* 1918, 33, 145.

<sup>21</sup> Karmilinos and Dittmer, *Proc. Soc. Exp. Biol. Med.* 1943, 53, (2), 111; *Imp. Bur. Dairy Sci. Abstr.* 1943, 5, 151.

<sup>22</sup> Zwangerman, *Proc. World's Dairy Congress*, 1931, Sect. 1, p. 172; *Amer. Chem. Abstr.* 1933, 27, 537.

<sup>23</sup> Davies, *Agric. Progr.* 1936, 13, 112; *Amer. Chem. Abstr.* 1936, 30, 4930.

<sup>24</sup> Bisenro and Belloni, *Chem. Zentr.* 1905, II, 63.

It should be noted that while the nitrogenous bodies enumerated in Table III have been identified in milk, it is possible that they are not all normally present; some may arise during its fractionation or as a result of bacterial action.

(iii) *The Nitrogenous Bodies associated with the Fat Globules.*

On the surface of the fat globules of milk there exists an adsorbed layer containing phosphatides, etc., but consisting largely of a protein which has been studied in some detail by several investigators. According to Wiese and Palmer (J. Dairy Sci. 1934, 17, 29) the protein is different from casein, lactalbumin, and lactoglobulin in its constituent amino-acids, the difference being confirmed by serological tests (Palmer and Lewis, Arch. Path. and Lab. Med. 1933, 16, 303).

(iv) *The Carbohydrates of Milk.*

The carbohydrates of milk consist almost entirely of lactose. It is present as an equilibrium mixture, the composition of which differs slightly from that obtaining in aqueous solution (viz. 1 part of  $\alpha$ -lactose as hydrate and 1.65 parts of  $\beta$ -lactose at room temperature), owing to the presence of the milk salts. The rather low solubility of lactose in water (7.3% at 15°C.), which is reduced in presence of sucrose, is of importance in the manufacture of condensed milk.

Some evidence has been recorded of traces of other sugars in milk besides lactose. Thus Whitnah (J. Amer. Chem. Soc. 1931, 53, 300) claims that there exists in milk 0.0-0.35% of glucose, while Jones (J. Dairy Res. 1936, 7, 41) found 0.06% (average value) of a fermentable sugar (possibly glucose) in normal milk.

Carbohydrates have been detected as constituents of the proteins of milk; thus Tillmann and Philippi (Biochem. Z. 1929, 215, 36, 50) found 0.36-0.55% in casein prepared by Hammersten's method and 1.3-1.5% in the albumin+globulin fraction. Sørensen and Haugegaard (Compt. Rend. Trav. Lab. Carlsberg, 1933, 19, No. 12) have further developed Tillmann and Philippi's method, and record the presence of 0.31% of galactose in Hammersten's casein and 0.44% in lactalbumin.

Milks of other mammals are claimed to contain carbohydrates with properties different from those of lactose, e.g., that in mare's milk is fermentable by yeast while, according to Polonovski and Lespagnol (Compt. rend. 1931, 192, 1319), human milk contains "gynolactose" and "allolactose" with rotatory powers less than that of lactose, the former also having a lower reducing power.

(v) *Inorganic Constituents.*

(a) *Major Constituents of the Ash.*—The composition of the ash of milk as reported by H. D. Richmond, "Diary Chemistry," 4th ed., revised by G. D. Elsdon and G. H. Walker, London, 1942,\* p. 20), together with the extremes and mean results of other observers, is given in Table IV. It will be noted that the sum of Richmond's figures exceeds 100%, owing to the fact that metals, which are present partly as chlorides, are calculated as oxides.

Although milk is nearly neutral (pH ca. 6.5), its ash is invariably alkaline in reaction. During incineration the loss of organic acid radicals

\* Later references in this article to Richmond refer to this book.

TABLE IV.

Constituent.	Richmond.	Various observers.	
	% wt./wt. of ash.		
		Extremes.	Mean.
P <sub>2</sub> O <sub>5</sub> . . .	29.33	21.57-29.33	25.67
CaO . . .	20.27	20.01-27.32	22.37
MgO . . .	2.80	2.25- 3.12	2.63
Cl . . .	14.00	13.57-16.38	14.44
SO <sub>3</sub> . . .	Trace	Trace- 4.11	3.39
Fe <sub>2</sub> O <sub>3</sub> . . .	0.40	0.05- 0.40	0.20
Na <sub>2</sub> O . . .	6.67	5.82-11.92	9.03
K <sub>2</sub> O . . .	28.71	25.63-30.33	26.34
CO <sub>2</sub> . . .	0.97	0.97	0.97
Less O≡Cl .	103.15		
	3.15		
	100.00		

(e.g., citrate and caseinate) is greater than the gain in acid radicals, e.g., ca. 8% of the phosphorus pentoxide and all the sulphur trioxide and carbon dioxide are derived from organic bodies. Approximate 70% of the ash of milk is insoluble in water and consists largely of the double phosphate CaKPO<sub>4</sub>, together with a small proportion of MgKPO<sub>4</sub>; the soluble portion of the ash (30%) consists mostly of alkali chlorides (Richmond, *op. cit.*, p. 21).

It is evident that the composition of the ash is not the same as that of the mineral constituents of the milk, which are considered in Section 4.

(b) *Trace Elements.*—The content of certain trace elements in milk is to some extent affected by the food ingested by the cow. Large increases in the iodine content of milk resulting from the feeding of iodine-rich rations have been

TABLE V.—TRACE ELEMENTS.

Element.	P.p.m. in milk.
Fe . . . . .	0.40-0.53 <sup>25</sup> ; 0.56 <sup>26</sup> ; 0.3 <sup>27</sup>
Cu . . . . .	0.14-0.17 <sup>25</sup> ; 0.13 <sup>26</sup> ; 0.09-0.17 (av. 0.12) <sup>28</sup>
Mn . . . . .	0.05-0.17 <sup>29</sup> ; 0.06-0.17 <sup>30</sup>
Pb . . . . .	0.02-0.04 <sup>31</sup>
Zn . . . . .	1.76-4.45 (av. 3.3) <sup>32</sup>
I . . . . .	0.100 <sup>32</sup> ; 0.145 summer, 0.060 winter <sup>34</sup> ; 0.42 <sup>35</sup>
B . . . . .	0.2 <sup>36</sup>
F . . . . .	Trace.
Si . . . . .	0.18-0.53 <sup>37</sup> ; 1.2-4.0 <sup>38</sup>
Al . . . . .	1.9 <sup>39</sup>

<sup>25</sup> Krauss and Washburn, Ohio Agric. Exp. Sta. Bull. No. 532, 1934, p. 63.

<sup>26</sup> Remy, Z. Unters. Lebensm. 1932, 64, 545.

<sup>27</sup> Kon, Chem. and Ind. 1943, 478.

<sup>28</sup> Sylvester and Lampitt, Analyst, 1935, 60, 376.

<sup>29</sup> Richards, Biochem. J. 1930, 24, 1572.

<sup>30</sup> Buttner and Miermeister, Z. Unters. Lebensm. 1933, 65, 644.

<sup>31</sup> Kasahara *et al.*, Jahrb. Kinderheilk. 1936, 147, 357.

<sup>32</sup> Sato and Murata, J. Dairy Sci. 1932, 15, 451.

<sup>33</sup> Leitch and Henderson, Biochem. J. 1926, 20, 1003.

<sup>34</sup> W. L. Davies, "Chemistry of Milk," London, 1939, p. 472.

<sup>35</sup> Foley, J. Dairy Sci. 1942, 25, Abstr. 56; Milk Dealer, 1941, 30, 39.

<sup>36</sup> Bertrand and Agulhon, Compt. rend. 1913, 156, 2027.

<sup>37</sup> Strohecker *et al.*, Z. Unters Lebensm. 1935, 70, 345.

<sup>38</sup> Kettmann, Milch. Forsch. 1927, 5, 73.

<sup>39</sup> Lehmann, Arch. Hyg. Bakt. 1931, 106, 309

reported (Kieferle *et al.*, *Milch. Forsch.* 1927, 4, 1; Lunde and Closs, *Norsk. Mag. Laegevidensk.* 1936, 97, 377); the results of feeding an iron-rich ration are contradictory, while copper in the feed has little effect on the copper content of the milk (*see also under* Section 11, "Off" flavours of Milk, p. 111*d*). The iodine content of colostrum is relatively high (up to 2.9 p.p.m. according to Miethke and Courth, *Milch. Forsch.* 1932, 13, 394), but during secretion rapidly falls to the normal value for milk (approximately 0.1 p.p.m.). The zinc content of colostrum (Sato and Murata, *J. Dairy Sci.* 1932, 15, 451) and also the silica content (Kettmann, *Milch. Forsch.* 1927, 5, 73) change in a similar manner to the iodine content.

It should be borne in mind that some of the trace elements found in milk may not be naturally present but may have been introduced during processing (*e.g.*, silicon, iron, copper, and tin). Typical recorded figures are given in Table V.

Spectrographic examination of milk ash has been made by several investigators, but the results are somewhat conflicting (*see* Dingle and Sheldon, *Biochem. J.* 1938, 32, 1078, who refer to papers by Wright and Papish, De, Blumberg, and Rask).

#### (vi) Miscellaneous Constituents.

TABLE VI.

- (1) Citrate . . . 0.07-0.4%, av. 0.18% (calc. as citric acid).  
 (2) Gases  $\text{CO}_2$  . . 10% by vol. in milk in udder, 5% immediately after milking, falling to 3%.  
 $\text{O}_2$  . . . Trace.  
 $\text{H}_2\text{S}$  . . . Trace in boiled milk.  
 (3) Cholesterol . . 0.0105-0.0176% (Dennis and Mhot, *J. Biol. Chem.* 1918, 37, 353).  
 (4) Vitamins . . . *See under* "Nutritional Value," p. 109*a*.

#### 4. PHYSICO-CHEMICAL RELATIONSHIP OF CONSTITUENTS. THE COMPLEX OF CASEIN WITH THE CALCIUM AND PHOSPHATE IN MILK.

It is generally agreed that the dispersed insoluble constituents of milk contain calcium phosphate (with a trace of magnesium phosphate), but opinions are divided as to whether this is present as di- or tri-calcium phosphate. The work usually quoted is that of Van Slyke and Bosworth (*J. Biol. Chem.* 1915, 20, 135; 1916, 24, 191), which indicates that milk contains either a mixture of dibasic calcium phosphate and calcium caseinate (containing eight equivalents of calcium) or tribasic calcium phosphate with an acid caseinate. As a result of a study of material separated on centrifuging (separator slime), these authors preferred the former alternative. Other workers have supported that view, but of more recent date Pyne (*Biochem. J.* 1934, 28, 940), Ling (*J. Dairy Res.* 1936, 7, 145; 1937, 8, 173), and Ramsdell and Whittier (*J. Biol. Chem.* 1944, 154, 413) have submitted evidence suggesting that the major portion of the colloidal phosphate in milk is in the form of  $\text{Ca}_3(\text{PO}_4)_2$ . It is doubtful whether there is any association, other than a purely physical one, between the casein and the colloiddally dispersed insoluble phosphate.

The reported distribution of calcium and phosphorus between (a) the dialysable and non-dialysable fraction, (b) the soluble and insoluble fractions after rennet treatment, and (c) the soluble and insoluble fractions after trichloroacetic acid treatment of milk is given in Table VII.

TABLE VII.—DISTRIBUTION OF CALCIUM AND PHOSPHORUS IN MILK.

(a) Separated milk. Lampitt *et al.* (*Biochem. J.* 1937, 31, 1861).

	% in non-fatty milk solids.	% of total present.
Dialysable inorganic P .	0.63-0.77	33-43
" organic P .	0.31-0.38	7-15
" Ca . . .	1.37-1.41	25-42
" Mg . . .	0.19-0.35	62-83

(b) Whole milk (0.112% total P and 0.130% total Ca) treated with rennet. Ling (*J. Dairy Res.* 1937, 7, 173).

% of total P.	
Soluble.	Insoluble.
Total . . . . . 51.1	Total . . . . . 48.0
Inorganic . . . . . 33.5	Inorganic . . . . . 30.0
Organic (ester P) . . 17.6	(27.7 as $\text{Ca}_3(\text{PO}_4)_2$ 2.3 as $\text{Mg}_3(\text{PO}_4)_2$ )
	Organic . . . . . 18.0
	(16.8 as casein 2.3 as phosphatides)

% of total Ca.	
Soluble.	Insoluble.
Total . . . . . 33.3	Total . . . . . 66.7
	(46.4 as $\text{Ca}_3(\text{PO}_4)_2$ 20.3 as casein)

(c) Whole milk (0.103% total P) precipitated with 8%  $\text{CCl}_3\text{COOH}$ . Graham and Kay (*J. Dairy Res.* 1933-34, 5, 51).

% of total P.		
	Acid-soluble.	Acid-insoluble.
Total P . . . . .	75	25
Inorganic P . . . . .	65	all
Organic P . . . . .	10 (ester P)	(as phosphatide 0.5) (as casein 18.5)

#### 5. FACTORS AFFECTING THE GENERAL COMPOSITION OF MILK.

(a) Breed of the cow has an effect on the milk which is perhaps most evident in its fat content. The latest and most authoritative published data are given in the Reports of the Livestock Improvement Scheme, 1937 and 1938 (*J. Min. Agric.* 1937, 44, 875; 1938, 45, 950), from which have been taken the average fat contents of many samples of milk from various breeds of cow during two twelve-monthly periods (*see* Table VIII).

It should be mentioned that the breed giving milk of the lowest fat content may give the highest yield of fat.

TABLE IX.—MONTHLY AVERAGE COMPOSITION OF MILK.

Month.	Fat, %.	Non-fatty solids, %.
January . . . . .	3.65	8.70
February . . . . .	3.58	8.77
March . . . . .	3.54	8.76
April . . . . .	3.52	8.73
May . . . . .	3.46	8.70
June . . . . .	3.44	8.70
July . . . . .	3.53	8.69
August . . . . .	3.60	8.68
September . . . . .	3.68	8.76
October . . . . .	3.80	8.82
November . . . . .	3.81	8.81
December . . . . .	3.75	8.78
Total average for 693,315 samples . . . . .	3.61	8.77

Highland Agric. Soc. Scotland, 1925, 37, 126). During drought conditions the protein and fat contents of the milk increase, and the lactose content decreases.

(i) Effect of Disease.—The first effect of ill health of the cow on the milk is usually a falling off in the yield, which may be followed by a change in the proportion of the constituents.

The effect of mastitis infection is to reduce the casein, fat, and lactose, and to increase appreciably the chloride content of the milk (Vanlandingham *et al.*, J. Dairy Sci. 1941, 24, 383). Much work of recent date has suggested that apparently healthy cows yielding milk of low non-fatty solids content may be suffering from sub-clinical mastitis (Rowland, J. Dairy Res. 1938, 9, 51). This has been supported by Foot and Shattock (*ibid.*, p. 166) and by Rowland and Zein-el-Dine (*ibid.*, p. 182) who showed that those quarters of the udders of the cows infected with *Str. agalactæ* (mastitis) gave milk with significantly lower non-fatty solids than uninfected ones. Sub-clinical *Staphylococci mastitis* infection reduces the casein content and increases the pH of the milk (Shattock and Mattick, *ibid.* 1940, 11, 311).

(j) Effect of Hormones.—As the result of much experimental work in recent years, it has been found possible to increase the yield of milk during declining lactation by administration of hormones. Coincident with this stimulation of the secretion of milk, the daily yield of butterfat may be increased as much as 50% by repeated injection of anterior pituitary extracts (Folley and Young, Biochem. J. 1939, 33, 192), and the yield of non-fatty solids by injection of thyroxine or by addition of dry thyroid to the feed (Folley and White, Proc. Roy. Soc. 1936, B, 120, 346). Oral administration of iodinated proteins (especially iodinated casein) has also been found to give increased yield of milk during declining lactation (Reineke and Turner, J. Dairy Sci. 1942, 25, 393). Oestrogens have the effect of inducing lactation in barren animals, but inhibit established lactation (Folley, Vet. Rec. 1944, 56, No. 2, 9). Restricted supplies of hormones have prevented their use on a large scale.

(k) Other Influences which affect the composition of the milk are *sexual excitement*, which often, but not invariably, results in a

temporary increase in fat content, and *milking by unskilled personnel*, which causes reduction in yield and in fat content of the milk.

## 6. RELATIONSHIP BETWEEN THE MILK CONSTITUENTS.

Studies on the variations in the percentage of the various constituents of milk from healthy cows show that usually, when the fat content increases, the protein, ash, and chloride contents also increase, while the lactose content decreases. In spite of these variations and those resulting from disease, the osmotic pressure of the milk (conveniently determined from the depression of the freezing-point) remains remarkably constant (*see* Section 7(b), p. 107a). From this it follows that one important relationship between the constituents of milk is determined by the constancy of the sum of the osmotic pressures of the individual constituents. The chloride and the lactose together account for approximately 80% of the total osmotic pressure, thus enabling formulae relating percentage of lactose (*L*) with that of chloride (as chlorine) (*C*) to be derived. Thus:

$44(L + C) = \text{a constant}$	(Kopatschek, Milch. Zentr. 1922, 51, 85).
$100C/L < 2$ usually	(Koesler, Landw. Jahrb. Schweiz. 1922, 36, 133).
$L > 7-10-6C$	(Mathieu and Ferné, Ann. Pâiss. 1914, 7, 12).
$L = 7.07-18C$	(Sundberg, Z. Unters. Lebensmittel, 1931, 62, 509).
Also $L = 6.6 \times \text{ash } \%$	(Boulin, Ass. Franc. pour l'avanc. sci. Strasbourg, 1920, 62).

\* This relationship has been the subject of much study on the Continent, and is applied to the detection of added water (*see* Joret and Rader, Ann. Pâiss. 1927, 20, 341, 403; Paget and Genel, *ibid.* 1931, 27, 157).

Certain relationships involving the protein content have also been proposed. Thus:

$L: \% \text{ protela} : \% \text{ ash}$ (Vleth's ratio) (Analyst, 1888, 13, 49, 63; 1891, 16, 203).
$\% \text{ Ash} = 0.1 \times \% \text{ protela}$ (Sherman, J. Amer. Chem. Soc. 1903, 25, 132).
$-0.38$

The distribution of the nitrogen of milk between the various protein constituents is as follows:

Nitrogen combined as	Percentage of total N.
Casein <sup>1</sup> . . . . .	76.5
Albumin <sup>2</sup> . . . . .	12.0
Globulin <sup>2</sup> . . . . .	6.0
Total protela <sup>2</sup> . . . . .	94.5

<sup>1</sup> Goldberg *et al.* (J. Dairy Res. 1932, 4, 48).

<sup>2</sup> Davies (*ibid.*, p. 142).

## 7. PHYSICAL PROPERTIES.

(a) Colour.—The colloidal calcium phosphate and caseinate and the emulsified fat are responsible for the white appearance of milk in reflected light and opacity in transmitted light. The creamy colour results from the presence of carotene in the fatty phase and riboflavin in the aqueous phase. When the fat rises, the aqueous layer appears by comparison with the cream layer to have a bluish tinge, the intensity of which increases as the fat content of the

aqueous layer decreases. Variations in the proportions of the constituents previously enumerated naturally affect the colour of the milk.

(b) **Surface Tension.**—The recorded figures show a range of 46.5–53.3 (most samples 49–52) dynes per cm. (Velu and Belle, *Compt. rend. Soc. Biol. Paris*, 1935, 119, 678). Dilution, skimming, and homogenising have little effect on the surface tension, but variations occur when the properties of the calcium caseinate are changed, e.g., by alteration of the pH.

(c) **Viscosity.**—While the viscosity of milk, as that of other liquids, varies with temperature, the presence of the fat globules introduces an additional effect dependent upon their size and form (tendency to form clumps on standing) and the plastic properties of the fat itself. The viscosity of whole milk is greater than that of separated milk and, with rise in temperature, decreases at a greater rate. Homogenisation of whole milk causes an increase, pasteurisation and freezing followed by thawing a decrease, in viscosity. There is no significant change in viscosity of separated milk at 20°C. with increasing acidity up to 0.45% (calculated as lactic acid). At higher acidities the viscosity increases, owing to increased hydration of the protein (Mohr and Oldenberg, *Milch. Forsch.* 1929, 8, 429, 576; Mohr and Moos, *ibid.* 1934, 16, 188; Bateman and Sharp, *J. Agric. Res.* 1928, 36, 647). Tapernoux and Vuillaume (*Compt. rend. Soc. Biol.* 1934, 115, 1128) reported that the viscosity of whole milk at 15°C. is 0.021 to 0.026 poises, and of separated milk 0.018 to 0.019 poises.

(d) **Electrical Conductivity.**—Wide variations are recorded in the conductivity of milk, Krenn (*Milch. Forsch.* 1933, 14, 513) giving values of  $38.0\text{--}68.4 \times 10^{-4}$  mhos, mostly  $41\text{--}50 \times 10^{-4}$  mhos. The conductivity shows little correlation with the amounts of the various constituents present in the milk, except in the case of the chloride content, with which it is approximately proportional (chlorides form the bulk of the soluble salts in milk). Niemeczycki and Galecki (*Lait*, 1938, 18, 1009) recommended determinations of conductivity of milk as a means of indicating abnormality, a value greater than  $54 \times 10^{-4}$  mhos being considered abnormal, suggesting mastitis infection. The conductivity of milk is also increased by the addition of neutralisers or ionisable preservatives.

(e) **Cataphoretic Behaviour.**—Under the influence of a direct electric current, not only the proteins, but also the fat globules of milk, migrate to the anode or cathode, according to the pH. Mohr and Brockmann (*Milch. Forsch.* 1931, 11, 211) found that the proteins and also the fat globules of milk migrate to the cathode at  $\text{pH} < 4.3$  and to the anode at  $\text{pH} > 4.3$ . Butter fat dispersed in water behaved similarly, except that the critical pH is 3.0, the difference being attributable to the protein adsorbed on the fat globules of milk. These authors stated that neither heating nor homogenisation affect the cataphoretic behaviour of the fat globules in milk.

(f) **Redox Potential.**—Buruiana (*Lait*, 1931, 12, 785) found that the  $E_h$  of milk is approxi-

mately +0.200 v., and may be reduced to ca. -0.200 v. by bacterial action and by heating. For the relationship between the development of "oxidised" flavour and the redox potential of milk, see Section 11, p. 112d.

(g) **Refractive Index.**—The refractivity of milk is an additive property of the soluble constituents. It is usually determined on the serum, the value obtained depending on the precipitant used for defecation, copper sulphate being generally used. Elsdon and Stubbs made a very thorough study (see papers in *Analyst*, 1927–30) of the refractive index of the copper sulphate serum of milk, and recorded values obtained by the Zeiss dipping-refractometer of 37–39 (average 38.3) for 997 samples (equivalent to refractive indices of 1.3415 to 1.3423, average 1.3420). These authors claim that 5% of added water may be detected in milk by this method. Tocher (*l.c.*) gives the same average value of 38.3 for 676 samples.

(h) **Specific Gravity.**—The presence of air bubbles in freshly drawn milk normally precludes the accurate determination of its sp.gr. until after the elapse of 1 hour after drawing. The sp.gr. increases slightly up to 12 hours after milking (Rechnagel phenomenon), owing to the change in sp.gr. of the fat during gradual solidification (Richmond, *op. cit.*, p. 85), or, according to Pynson and Dahle (*J. Dairy Sci.* 1938, 21, 601), to an increase in the amount of bound water in the lyophilic colloids. Determinations of the sp.gr. of milk are therefore made after the elapse of several hours (ca. 12) after drawing. Recorded values for skimmed milk vary between 1.032 and 1.0365 at 15°C., and for whole milk of normal fat content from 1.028 to 1.034 (average 1.032), although individual cows may give milk with sp.gr. between 1.0135 and 1.0397. Tocher (*l.c.*) records the sp.gr. distribution frequency of 676 samples which gave values between 1.025 and 1.036.

Several formulæ have been evolved, relating total solids content ( $T$ ), fat content ( $F$ ), and specific gravity ( $S$ ) of milk. Richmond (*op. cit.*, p. 122) gave  $T = 0.25 \times 1,000(S - 1) + 1.2F + 0.13$ , and constructed a slide-rule from which sp.gr., fat content, or total solids content may be computed when two of the values are known.

(i) **Specific Heat.**—The recorded value for the specific heat of skimmed milk at normal temperature is 0.95, and for whole milk 0.92 up to 10°C., 0.95 at approximately 20°C., 0.93 at 30–50°C., and 0.94 at 60°C. The high value at 20°C. for whole milk is due to the effect of the latent heat of fusion of the fat (Bowen, U.S. Dept. Agric. Misc. Publ. 138, 1932).

(j) **Boiling Point.**—From the known cryoscopic and ebullioscopic constants of water and the average freezing-point depression of milk, the elevation of the boiling-point of milk may be calculated to be approximately 0.15°C. Bowen (*l.c.*) records, however, a determined boiling-point of 100.55°C./760 mm. The boiling-point is affected by the amount of calcium phosphate and citrate deposited during heating.

(k) **The Osmotic Pressure of milk** is its most constant property, being unaffected by the breed of cow, period of lactation, feed, season, etc. It is the sum of the osmotic pressures of

the milk constituents and amounts to 6.78 atm., according to Coste and Shelbourn (Analyst, 1919, 44, 158), who also indicate the proportion due to each constituent, the lactose and the chlorides contributing the major proportion. It follows from the constancy of the value that any change in the proportion of one constituent is accompanied by a change in others, e.g., when the lactose content falls the chloride content rises.

(l) **The Depression of the Freezing-Point  $\Delta$**  (the difference between the freezing-point of milk and that of water), being a function of the osmotic pressure, is equally constant. Its determination affords therefore a convenient means by which to estimate water added to milk. Exhaustive studies of the method of determining  $\Delta$  made by Monier-Williams (Food Report No. 22, H.M.S.O., 1914; Analyst, 1933, 58, 254) and by Elsdon and Stubbs (*ibid.* 1930 and 1933-36; J.S.C.I. 1931, 50, 135r) have led to the fairly general adoption of the Hortvet method prescribed by the Association of Official Agricultural Chemists ("Methods of Analysis," 1930, p. 275). The range of figures quoted in the literature for  $\Delta$ , obtained by different techniques, is 0.490-0.748°c. (extremes), and the normal range 0.512-0.580°c., average values being 0.537-0.570°c. Some of the higher recorded results may be due to the fact that increase of acidity of milk increases its  $\Delta$ . Elsdon and Stubbs (Analyst, 1934, 59, 140) gives  $\Delta$  values of 0.529-0.563°c. for 1,000 fresh, genuine samples, the average being 0.544°c. These authors state that milk with  $\Delta$  0.53° or above should be considered genuine, and that the presence of 5% of water added to normal milk may readily be determined by this method.

(m) **pH.**—The usual pH range of fresh milk is

6.4-6.9 (average 6.6), but the figure varies according to the condition of the udder of the cow and to the effects of micro-organisms present in the milk. The pH is increased by dilution and reduced by heating.

(n) **Buffer Capacity and Acidity.**—Milk has a strong buffer capacity, attributable largely to the proteins, the citrate, and the phosphate present. At pH 6.5 the buffer capacity is greatest and at pH above 8.5 it is least. The buffering effect at the lower pH is due largely to the phosphates and at the higher pH to the proteins.

The acidity of normal milk as determined by titration with sodium hydroxide, using phenolphthalein as indicator, is 0.14-0.18% (calculated as lactic acid); a figure of ca. 0.19% for genuine milk indicates incipient souring, and below 0.13% suggests that the milk has been derived from unhealthy cows (Vaillant, Lait, 1935, 15, 961). The phenolphthalein end-point is not sharp, owing to the slow precipitation of tricalcium phosphate (Summer and Menes, J. Dairy Sci. 1931, 14, 136). The fading may be minimised by dilution of the milk, when the titration figure is reduced, or it may be prevented by addition of potassium oxalate before titration to remove calcium from solution, when the titration figure is reduced to a degree dependent on the amount of oxalate added (Pyne, Biochem. J. 1934, 28, 940).

## S. ENZYMES.

(See Table X.)

The enzymes of milk consist of native enzymes, i.e., those present in the milk in the udder, and enzymes originating from contaminating bacteria.

TABLE X.—ENZYMES PRESENT IN MILK.

Enzyme.	Substrate.	Pre-formed in milk.	Due to bacteria.	Conditions for in-activation.	Optimum pH.	Optimum temperature.	Product of reaction.
(a) <i>Esterases.</i>							
(i) Lipase.	Fat: butyric esters.	+	?	63°, 20 min.	8.0	—	Fatty acid.
(ii) Phosphatase.	P esters.	+	—	63-65°, 15 min.; immediately at > 75°.	9.0	—	Inorganic phosphate.
(b) <i>Protease.</i>							
Galactase.	Protein.	+	—	72-80°	6.4-7.2	37-42°	Peptones.
(c) <i>Carbohydrases.</i>							
(i) Lactase.	Lactose.	?	—	—	6.0	—	Glucose + galactose.
(ii) Amylase.	Starch.	+	+	60-65° 1 hour.	5.8-6.2	30°	Dextrin and reducing sugar.
(d) <i>Dehydrogenases.</i>							
(i) Reductase.	Methylene Blue; Resazurin.	—	+	—	5.5-8.5	—	Leuco-compounds.
(ii) Schardinger enzyme.	Methylene Blue and formaldehyde.	+	—	75° pH < 4 or > 9	8.0	40°	Leuco-compounds and formic acid.
(iii) Xanthine oxidase.	Methylene Blue and Xanthine.						Leuco-compounds and uric acid.
(e) <i>Oxidases.</i>							
(i) Peroxidase.	H <sub>2</sub> O <sub>2</sub> .	+	?	70-83°	4-6	—	Active oxygen
(ii) Catalase.	H <sub>2</sub> O <sub>2</sub> .	+	+	pH < 3 or > 10 90-92° 20 min.	7.0	—	Molecular oxygen



## (a) Esterases.

(i) *Lipase*.—The butyric rancidity of milk and milk products has been shown to be due to the action of a lipolytic enzyme (or enzymes) present in milk, capable of hydrolysing butter fat (also other fats and butyric esters), producing free acid. Whether the hydrolysis of these different substrates is due to one enzyme alone is not known. Mattick and Kay (J. Dairy Res. 1938, 9, 58) showed that a lipolytic enzyme is native to milk and used, for its determination, its hydrolysing action on tributyrin.

The lipolytic activity of milk is very variable and depends on the season of the year (highest in winter) and the stage of lactation of the cow (Hileman and Courtney, J. Dairy Sci. 1935, 18, 247). The activity is not prevented by freezing the milk, but is inhibited by high acidity, by heat (e.g., in pasteurisation), by heavy metals (especially copper) in presence of oxygen (Krukovsky and Sharp, *ibid.* 1940, 23, 1119). Agitation or homogenisation of the milk increases the fat-water interface and so produces a condition more favourable to lipolysis (*idem*, *ibid.* 1938, 21, 671). The enzyme is destroyed by heating at 63°C. for 20 minutes (Csiszar, Milch. Forsch. 1933, 14, 288).

(ii) *Phosphatase*, an enzyme capable of hydrolysing phosphoric esters, is native to milk, its activity varying with the stage of lactation. Its association with the protein adsorbed on the fat globules has been suggested (Grabam and Kay, J. Dairy Res. 1933, 5, 54, 63). The phosphatase is active over the pH range 6–10, with an optimum at 9.0. During the pasteurisation of milk, the most resistant of the pathogenic bacteria present are completely destroyed before the phosphatase, and consequently determination of phosphatase activity in the milk affords a useful method for testing the efficiency of the pasteurisation process. The method most generally applied is based on the determination of the phenol liberated by the action of the phosphatase on diphenyl phosphate (Kay and Grabam, *ibid.* 1935, 6, 191). It is claimed that, by this method, it is possible to detect the presence of 0.25% of raw milk in pasteurised milk, and in "holder" pasteurised milk to detect whether the holding time (30 minutes) has been reduced by 10 minutes, or the temperature (145°F.) has been lowered by 1.5°F. (see "Pasteurisation," p. 113b).

(b) *Protease*.—Thatcher and Dahlberg (J. Agric. Res. 1917, 11, 437) describe an enzyme (*galactase*) present in milk, not of bacterial origin, which slowly breaks down milk protein to peptones and simpler substances. It is probably of tryptic nature and is most active at pH 5.4–7.2 and at 30–42°C. The action is inhibited at low temperatures and in the presence of 15% of sodium chloride (it is not active in salt butter), and destroyed at 72–80°C., according to the pH of the medium.

## (c) Carbohydrases.

(i) *Lactase*.—Vandeveld (Biochem. Z. 1908, 11, 61) demonstrated the presence in milk of very small quantities of an enzyme which hydrolyses lactose to glucose and galactose. Svanberg (Z. physiol. Chem. 1930, 188, 207), however, failed to find it in normal milk.

(ii) *Amylase* is native to milk, being probably derived by infiltration from the blood stream by way of the mammary gland (Grimmer, Biochem. Z. 1913, 53, 429). Bacteria present in milk also secrete the enzyme. On precipitating casein, part of the enzyme accompanies the precipitate, a small amount being left in the whey. Its activity, which is affected by the salts present (especially the chloride), is optimal at 30°C. and pH 5.8–6.2, under which conditions the enzyme in 100 ml. of milk is capable of hydrolysing 50–100 mg. of gelatinised starch. The enzyme may be inactivated by heating at 60–65°C. for 1 hour (Heiduschka and Komm, Z. physiol. Chem. 1931, 196, 187). The amylase content is high in milk from diseased udders and also in colostrum up to the fourth day after parturition. The estimation of amylase was suggested by Giffhorn (Milch. Zentr. 1911, 7, 236) as a means of determining the bacterial condition of milk, and for detecting the presence of milk from diseased cows; Gould (J. Dairy Sci. 1932, 15, 230) used this method for testing efficiency of pasteurisation.

(d) *Dehydrogenases*.—Freshly drawn milk has very little reducing action on Methylene Blue or Resazurin, but this property develops as the number of bacteria increases owing to their *reductase* activity. This is the basis of one method used for determination of the bacterial quality of milk (see Section 10, p. 111d).

There is also present in milk a native enzyme known as *aldehydease* or *Schardinger enzyme*, which reduces Methylene Blue in presence of formaldehyde. In addition, adsorbed on the fat globules of milk, there is a third enzyme (*xanthine oxidase*) which, in presence of Methylene Blue (or of nitrates), oxidises certain purines, e.g., xanthine, to uric acid (Morgan *et al.*, Proc. Roy. Soc. 1922, B, 94, 109; Dixon and Thurlow, Biochem. J. 1924, 18, 971, 976, 988). Later Booth (*ibid.* 1938, 32, 494) concluded that the two last-named enzymes are most probably identical. The Schardinger enzyme activity is weakened by heating to 70°. It is inactivated at 75°C., at pH <4 and >9, in presence of silver, copper, or mercury, and in sunlight or ultraviolet light. The conditions for maximum activity are 40° (Toyama, Amer. Chem. Abstr. 1934, 28, 7279) and pH 8 (Basu and Mukherjee, J. Indian Chem. Soc. 1936, 13, 11). Schardinger enzyme is not present in human milk (Sassenhagen, Arch. Kinderheilk. 1910, 53, 281), or in goats' milk (Wedemann, Biochem. Z. 1914, 60, 330).

## (e) Oxidases.

(i) *Peroxidase* is a native enzyme of milk associated with the lactalbumin. This enzyme liberates active oxygen from hydrogen peroxide and is usually estimated by the Storch reaction (development of blue colour with hydrogen peroxide and *p*-phenylenediamine). Peroxidase is inactivated at 70–83°C., according to the time of heating (e.g., 1 hour at 70°C., or 5 minutes at 75°C., J. E. Lane-Clayton, "Milk and its Hygienic Relations," London, 1916, p. 85), and destroyed at pH >10 and <3, although if the pH change is immediately followed by neutralisation the activity is restored. Traces of hydrogen sulphide or sulphhydryl compounds



present in boiled milk inhibit the activity of the enzyme.

(ii) *Catalase*, which liberates molecular oxygen from hydrogen peroxide, is native to milk, the content being related to the catalase content of the blood of the cow (Zeilinger, *Biochem. Z.* 1933, 257, 450). The amount of catalase present in milk varies with the breed of the cow and depends on the fraction of milking, being richest in the strippings. The enzyme, which is precipitated with the casein on rennet coagulation of milk, has optimum activity at pH 7. Complete inactivation of the enzyme occurs in 20–30 minutes at 90–92°C., but at lower temperatures longer times are required.

Leucocytes, from diseased udders, and bacteria increase the catalase content of milk. Determination of catalase, e.g., by measurement of the volume of oxygen liberated from hydrogen peroxide or by iodometric determination of the hydrogen peroxide decomposed (Anderson and McWalter, *J.S.C.I.* 1937, 56, 270r) has been suggested as a means of determining such contamination, but the methods are at best only empirical.

#### 9. NUTRITIONAL VALUE.

(a) *General*.—Milk is a perfect food for infants up to 6 months of age, after which supplements are required for normal growth. The energy contributed by the major constituents is indicated in Table XI.

TABLE XI.—100 g. WHOLE MILK.

	g.	Energy value.
Fat . . . . .	3.75	33.8 kg.-cal.
Protein . . . . .	3.2	12.8 "
Carbohydrate . . . . .	4.7	19.8 "
Calcium . . . . .	0.12	
Iron . . . . .	0.0010	
Phosphorus . . . . .	0.034	
Total .		66.4 kg.-cal.

The proteins present are biologically complete and have a supplementary action to cereal proteins (Kon, *Chem. and Ind.* 1943, 478). The fat, present as small globules, is precipitated with the casein during digestion and is thus in an easily assimilable form. The lactose constituent of milk, apart from its energy value, is important by virtue of its controlling influence on the intestinal bacterial flora (Gerstley *et al.*, *Amer. J. Dis. Child.* 1932, 43, 555), and the fact that it increases the adsorption of calcium and phosphorus in the intestine in a manner similar to that of vitamin-D (Roberts and Christman, *J. Biol. Chem.* 1942, 145, 267).

As a source of calcium and phosphorus (Table XI), so essential in childhood, milk is of considerable importance, as it provides a necessary supplement to sugars, cereals, and tubers which are deficient in these elements. The inclusion of regular quantities of milk in children's diet has been shown to result in enhanced increase in weight and improved health (Morgan *et al.*, *Amer. J. Dis. Child.* 1927, 33, 404; 1928, 36, 972).

Whether pasteurisation, deemed necessary by

health authorities to safeguard public health, causes loss of nutritive value has been the subject of much controversy. The subject has been complicated by prejudice and by conflicting evidence arising from shortcomings in the planning of experiments, and also, in the earlier experiments, from inadequate knowledge of the significance of vitamins in the diet. Recent large-scale studies made in this country have confirmed the findings of Morgan *et al.* (*l.c.*) and also show that there is no significant difference in nutritive value between raw and pasteurised milk (Milk Nutrition Committee, "Milk and Nutrition," Reading, 1938).

(b) *The Ease of Digestion* of cows' milk is generally compared with that of human milk, as this property is of major importance in infant feeding. The first stages in the process of digestion entail the conversion of the caseinogen to casein, which precipitates in the presence of the calcium ion of the milk as a curd (calcium caseinate). As the casein of cows' milk is associated with a relatively smaller proportion of protective colloid (lactalbumin and lactoglobulin) and more calcium ion than that in human milk, the former precipitates in a very much coarser form than does the latter, and so the subsequent digestion proceeds more slowly. The state of division of the casein curd from milks of different cows is not by any means constant. Some milks, termed "soft-curd milks" produce a fine and friable curd during digestion (these usually have low casein, total protein, and ash contents) while others, "hard-curd milks," produce a coarse and rubbery one. The latter are chosen for cheese making and the former, being more easily digested, are preferred for infant feeding.

In view of the need for differentiating milks according to the types of curd they produce, an empirical method has been devised for determination of the consistency of the curd (curd tension) produced by treatment of milk with a pepsin-hydrochloric acid mixture [Miller's modification (*J. Dairy Sci.* 1935, 18, 259) of Hill's method (*ibid.* 1923, 6, 509), adopted by the American Dairy Science Association Committee on Methods, 1938, and quoted by Doan (*ibid.* 1938, 21, 739)]. Curd tension is not affected by "holder" pasteurisation, but it is reduced by homogenisation or prolonged heat-treatment, e.g., sterilisation. Processes suggested for the preparation of soft-curd milk include

- (i) the addition of sodium hexametaphosphate, pyrophosphate, or citrate (Tracy and Corbett, *ibid.* 1940, 23, 289);
- (ii) superheating followed by centrifuging to remove insoluble protein (Dizikes and Doan, *ibid.* 1942, 25, 37);
- (iii) sonic treatment (Bikoff *et al.*, *New York Sta. J. Med.* 1941, 41, 2052);
- (iv) use of proteolytic enzymes (Blatt *et al.*, *J. Pediat.* 1940, 17, 435).

The digestion of the casein of milk has been studied under conditions comparable with those in the digestive tract (Flora and Doan, *J. Dairy Sci.* 1938, 21, Abstr., 163; see also Bull. Pa. Agric. Exp. Sta. No. 380, 1939, quoted by Dizikes and Doan, *J. Dairy Sci.* 1942, 25, 38),

and it has been proposed to use the curd particle-size as a measure of the ease of digestion (Storrs, *ibid.* 1941, 24, 865; Wolman, 30th Ann. Conv. Internat. Assoc. Milk Dealers, Lab. Sect. Proc., p. 114, 1937; J. Dairy Sci. 1938, 21, Abstr., 243).

(c) Vitamins.—Table XII shows the wide

range of values for the vitamin content of milk recorded in the more recent literature. Column 1 gives the values for milk of pasture-fed cows (summer milk) and column 2 for milk of stall-fed cows (winter milk). The results in column 3 are for milk from cows having unspecified types of feed. Vitamin-A in milk is almost entirely confined

TABLE XII.

Vitamin.	Vitamin units.	1.	2.	3.	Effect of heat.
<i>Fat-soluble.</i>					
-A. Liquid milk.	I.U. per ml.	1.05-2.35 <sup>1</sup>	0.42-2.79 <sup>1</sup>	0.1-2.20 <sup>2</sup>	} Stable. <sup>24</sup>
Butterfat.	I.U. per g.	29-85 <sup>3, 4</sup>	7.4-40 <sup>3</sup>	17.9-24.6 <sup>2</sup>	
-D. Liquid milk.	I.U. per ml.	0.024-0.038 <sup>2</sup>	0.003-0.017 <sup>2</sup>	0.003-0.05	} Stable. <sup>20</sup>
Butterfat.	I.U. per g.	0.83-0.99 <sup>5</sup>	0.07-0.23 <sup>6</sup>	—	
-E			Traces <sup>7</sup>		Unstable on evaporation. <sup>21</sup>
-K			Traces <sup>8</sup>		Probably unstable on evaporation. <sup>21</sup>
<i>Water-soluble.</i>					
-B <sub>1</sub> (Aneurin).	μg. per g.	—	—	0.15-0.70 <sup>2, 9</sup>	10-20% loss on pasteurisation <sup>9</sup> ; 30-40% loss on sterilisation; 10% loss on spray drying. <sup>23</sup>
-B <sub>2</sub> (Riboflavin).	μg. per g. mg. per 100 ml.	1.62-2.37 <sup>10</sup> —	1.42-2.18 <sup>10</sup> —	0.27-3.0 <sup>2</sup> 0.17-4.3 <sup>4</sup>	Stable. <sup>9</sup> 20-30% loss on "holder" pasteurisation; very little loss on "H.T.S.T." pasteurisation <sup>19</sup> ; 50% loss on sterilisation; 20% on drying. <sup>22</sup>
-P	—		Not found. <sup>11</sup>		—
-B <sub>2</sub> Complex.					
Nicotinic acid.	mg. per 100 g.	—	—	0.019-0.50 <sup>12, 14</sup>	—
Pantothenic acid.	mg. per 100 g.	—	—	0.17-0.70 <sup>12, 16</sup>	—
Biotin.	μg. per 100 g.	—	—	0.7-11.0 <sup>12, 15</sup>	—
Inositol.	mg. per 100 g.	—	—	3-39 <sup>12, 17</sup>	—
Pyridoxine.	μg. per 100 g.	—	—	2.6-17.0 <sup>12, 13</sup>	—
Folic acid.	μg. per 100 g.	—	—	<5; 15 <sup>12, 18</sup>	—

<sup>1</sup> Booher and Marsh, Tech. Bull. U.S. Dept. Agric. No. 802, 1941.

<sup>2</sup> Fixsen and Roscoe, Nutr. Abs. 1940, 9, 795.

<sup>3</sup> Dornbush *et al.*, J. Amer. Med. Assoc. 1940, 114, 278.

<sup>4</sup> Morton *et al.*, J.S.C.I., 1941, 60, 310T.

<sup>5</sup> Wilkinson, Analyst, 1939, 64, 17.

<sup>6</sup> Morgan and Pritchard, *ibid.* 1937, 62, 354.

<sup>7</sup> Mason and Bryan, J. Nutrition, 1940, 20, 501.

<sup>8</sup> Buriana, Compt. rend. 1940, 210, 721; J. Dairy Res. 1943, 13, 224.

<sup>9</sup> Houston *et al.*, J. Dairy Res. 1940, 11, 145.

<sup>10</sup> Hand and Sharp, J. Dairy Sci. 1939, 22, 779.

<sup>11</sup> Neuweiler, Z. Vitaminforsch. 1939, 9, 338.

<sup>12</sup> Various authors, Univ. Texas Publ. 1942, No. 4137, 112.

<sup>13</sup> McElroy and Goss, J. Nutrition, 1940, 20, 541.

<sup>14</sup> Bacharach, Nutr. Abs. 1941, 10, 459.

<sup>15</sup> Lampen *et al.*, J. Nutrition, 1942, 23, 11.

<sup>16</sup> Strong *et al.*, Ind. Eng. Chem. [Anal.] 1941, 13, 566.

<sup>17</sup> Woolley, J. Biol. Chem. 1941, 140, 453.

<sup>18</sup> Williams, J. Amer. Med. Assoc. 1942, 119, 1.

<sup>19</sup> Woessner *et al.*, J. Dairy Sci. 1940, 23, 1131.

<sup>20</sup> Weckel, *ibid.* 1941, 24, 445.

<sup>21</sup> Anderson *et al.*, Proc. Soc. Exp. Biol. Med. 1939, 42, 760.

<sup>22</sup> Houston *et al.*, J. Dairy Res. 1940, 11, 67.

<sup>23</sup> Henry *et al.*, *ibid.* 1939, 10, 272.

to the fatty phase, the proportion present in the fat varying little with the breed of the cow, but it is considerably affected by the feed, *e.g.*, it can be increased by feeding a diet rich in carotene or vitamin-A.

The vitamin-D content of milk may be increased by irradiation (when vitamins-A and -C are largely destroyed) or by feeding the cows with a ration rich in vitamin-D, *e.g.*, containing irradiated yeast.

Vitamin-B<sub>1</sub> (aneurin) is confined to the aqueous phase of milk, the content varying little with season, breed, or feed of the cow.

Vitamin-B<sub>2</sub> (riboflavin) shows some seasonal variation in milk, and although very stable to heat is rapidly destroyed when milk is exposed to light [*e.g.*, 40% of the vitamin-B<sub>2</sub> activity is lost when milk in glass milk-bottles is exposed for 1 hour to sunlight (Peterson *et al.*, J. Amer.

Chem. Soc. 1944, 66, 662)]. Little is known regarding the vitamin-B<sub>2</sub> complex, but there is evidence that pantothenic acid, pyridoxine, and biotin are synthesised by the cow (mostly in the rumen), as also is vitamin-B<sub>1</sub> (Wegner *et al.*, Proc. Soc. Exp. Biol. Med. 1940, 45, 769; 1941, 47, 90).

Milk is a poor source of vitamin-C (ascorbic acid), and the amount present is independent of the feed of the cow. As vitamin-C is easily destroyed by oxygen, light, and heat, especially in the presence of metals, particularly copper, losses on processing milk are rather large unless special precautions are taken, such as de-aeration and avoidance of contamination by metals. Pasteurisation by the H.T.S.T. process (*v. p.* 113c) is claimed to cause less vitamin-C destruction than the "holder" process (Woessner *et al.*, J. Dairy Sci. 1940, 23, 1131).

## 10. BACTERIOLOGY OF MILK.

The bacterial flora of milk may be subdivided in the following manner:

(a) *Flora of Milk from Cows with Normal Udders*, i.e., organisms present in milk drawn from healthy cows under aseptic conditions. These organisms probably originate from external sources and multiply in the teat canals between milkings, with the result that they are found chiefly in the fore-milk. The number of such organisms is not large, but it increases rapidly at slightly elevated temperatures. These bacteria are mostly micro-cocci which have little obvious action on milk. Of the other organisms present some produce alkali (*Bact. alcaligenes*), while others produce acid and peptonise the milk. The presence of *Str. liquefaciens*, *Str. thermophilus* (Orla-Jensen, "Dairy Bacteriology," London, 1931, p. 69), and staphylococci (G. S. Wilson, "Bacteriological Grading of Milk," H.M.S.O., 1935) has been reported.

(b) *Flora of Milk from Diseased Cows*.—The most important organisms are streptococci (in-

cluding *Str. agalactiae* or *mastitidis*), *Brucella abortus*, and *Mycobacterium tuberculosis*.

(c) *Flora introduced into Milk during Milking*.—These organisms include *B. coli*, *B. aerogenes*, *Proteus*, *Pseudomonas*, butyric bacilli from dung, lactic acid bacteria from water used for washing pails, etc., and moulds and yeasts from bedding materials in the stalls. Some of these organisms are thermophilic.

(d) *Pathogenic Flora derived from Human Sources (the Milker)*.—These originate from infected persons and carriers, and include streptococci, *Salmonella* (typhoid-paratyphoid) group organisms, *Corynebacterium diphtheriae*, and *Mycobacterium tuberculosis*.

The present system of distribution of bulked milk results in widespread outbreaks of disease should any contaminated milk be included. An analysis of such epidemic outbreaks is given in Table XIII, showing the figures of Wilson (Lancet, 1933, ii, 829) covering outbreaks in Great Britain from 1912 to 1931, and those of Armstrong and Parran (quoted by W. W. C. Topley and G. S. Wilson, "Principles of Bacteri-

TABLE XIII.—MILK-BORN EPIDEMICS.

Disease.	Organisms responsible.	Wilson.		Armstrong and Parran.		Deaths.
		Total number of out-breaks.	Number of persons affected.	Total number of out-breaks.	Number of persons affected.	
Scarlet fever . .	Hemolytic streptococci (especially <i>pyogenes</i> ).	31	3,057	40	3,030	20
Septic sore throat .	Ditto.			42	21,015	139
Diphtheria . . .	<i>C. diphtheriae</i>	13	732	26	971	7
Typhoid fever . . .	<i>B. typhosum</i>	25	1,843	470	14,068	219
Paratyphoid fever .	<i>B. paratyphosum</i> A and B			7	434	15
Dysentery . . .	<i>B. shigae</i> or <i>fleischeri</i>	12	3,750	6	92	5
Gastroenteritis .	<i>B. enteritidis</i> and <i>Staph. aureus</i> .			—	—	—

ology and Immunity," 2nd ed., London, 1936, p. 1599) on outbreaks in the U.S.A. from 1906 to 1926. The numbers of people affected, shown in this Table, are probably underestimated; sporadic outbreaks are not included, nor are cases of bovine tuberculosis or undulant fever (due to *Brucella melitensis* or *abortus*). Further analyses of American epidemics (during 1923-37) are given by Merchant (J. Milk. Tech. 1939, 2, 110) and by Crumbine (Reports to Conference of State and Provincial Health Authorities of North America 1932 and 1933; from associates of L. A. Rogers' "Fundamentals of Dairy Science," New York, 1935, p. 300).

Procedures adopted for bacteriological control of milk include the elimination of unhealthy cows, milking under strictly sanitary conditions by persons free from disease, adequate cooling of the milk after drawing, and efficient pasteurisation (v. p. 113b), followed by filling into sterile containers.

**Tuberculin - tested, Accredited, and Pasteurised Milk.**—By the provisions of the Milk (Special Designations) Order, 1936 and 1938, standards were prescribed (Table XIV) for these special milks, special licences being required for their production and sale.

**Bacteriological Testing of Milk.**—The methods applied to milk are direct microscopical count, plate count, coliform count, Breed-smear test, and Methylene Blue (or, more recently, Resazurin) reduction. Wilson and his associates ("Bacteriological Grading of Milk," H.M.S.O., 1935) made a critical study of the applicability of most of these methods and concluded that for rapid tests the Breed-smear method and the Methylene Blue reduction method were the most satisfactory [the latter method was officially adopted for testing milk samples under the Milk (Special Designations) Order, 1936-41]. More recently the Resazurin test has been advocated in preference to the Methylene Blue test, as it gives results much more rapidly and is therefore of greater value for the grading of milk (see J. G. Davis and S. T. Rowland, "Food Industries Manual," L. L. Hill, London, 1943, p. 225, for a description of this method).

## 11. "OFF" FLAVOURS OF MILK.

These flavours, which are described in the literature by a multiplicity of terms, may be divided into three main classes according to the cause of their development.

TABLE XIV.—GRADES OF MILK.

Grade of milk.	Conditions of production.	Bacteriological standard.	Remarks.
Tuberculin-tested (T.T.).	All herds to be kept separate and each animal submitted to a tuberculin test and to veterinary examination at intervals of not more than 6 months.	Must not reduce Methylene Blue in $\frac{1}{2}$ hours in May–October or $5\frac{1}{2}$ hours in November–April. No coli in 0.01 ml. ( <i>see</i> Note 1).	If bottled where produced called “T.T. (Certified).”
Tuberculin-tested Pasteurised (T.T. pasteurised).	Ditto.	Not more than 30,000 bacteria per ml. ( <i>see</i> Notes 1 and 2).	—
Accredited.	Each animal in the herd to be submitted to veterinary examination every 3 months; herds to be kept separate.	As T.T. ( <i>above</i> ).	If bottled where produced called “Accredited (Farm Bottled).”
Pasteurised.	Held for at least 30 mins. at 145–150°F. and then immediately cooled to 55°F. ( <i>see</i> Note 3). The milk must not be so heated more than once.	Not more than 100,000 bacteria per ml. ( <i>see</i> Notes 1 and 2).	Indicating and recording thermometers to be provided in plant which must be approved by the local authority.

Note 1.—As tested by the method specified in “Bacteriological Tests for Graded Milk” (Memo. 139, H.M.S.O., 1937).

Note 2.—Pasteurised milk must also pass the Phosphatase and Methylene Blue tests carried out as described in the Heat-treated Milk (Prescribed Tests) Order, 1944.

Note 3.—As a provisional measure (1941) pasteurisation may also be effected by the “High Temperature, Short Time” (H.T.S.T.) process, in which milk is held for at least 15 seconds at a temperature of not less than 162°F. and then immediately cooled to 55°F. In this case the plant must be thermostatically controlled and be provided with a device to divert automatically any insufficiently heated milk.

(a) Foreign Flavours from Natural Sources present in the freshly drawn milk may originate from the feed of the cow or the environment during milking. Chamomile, mint, thyme, garlic, and clover, when ingested by the cow, have all been claimed to give their characteristic flavour to the milk (Leitch, Scot. J. Agric. 1932, 15, 167, 314), while the feeding of sugar-beet tops leads to a fishy flavour due to trimethylamine oxide derived from betaine present in the feeding-stuff (Trout, 30th Ann. Conv. Intern. Assoc. of Milk Dealers, Lab. Sect., 1937, p. 131; J. Dairy Sci. 1938, 21, Abstr., 256). A salt flavour is evident in milk drawn late in the lactation period when the sodium chloride content is high, and also in milk drawn from cows with inflamed udders.

(b) Flavours which Develop during Storage.

(i) “Oxidised” flavour is the term which now generally supersedes such terms as “cardboard,” “metallic” flavour, etc., as it has been indicated that the effect is the result of oxidation. This flavour (which is normally confined to winter milk of low bacterial count) develops over a period of 1–3 days during storage at low temperature (3°C.). It appears only in certain milks and of these there are two types in which the flavour develops either spontaneously, or only when the process is catalysed by certain metallic ions, e.g., copper and ferric iron. Investigations of recent years indicate that when the undesirable flavour develops it is the phosphatide fraction of the adsorbed layer on the fat globules which becomes oxidised, as evidenced by a reduction in iodine number (Swanson and Sommer, J. Dairy Sci. 1940, 23, 201). The mechanism of the oxidation is not at present

known, but Olson and Brown (*ibid.* 1942, 25, 721, 1027) suggest that, in the case of the development of copper-catalysed flavour, phosphatides are oxidised by hydrogen peroxide, which has been shown to be formed by a reaction between ascorbic acid (or glutathione) and copper ions in presence of oxygen (Barron *et al.*, J. Biol. Chem. 1935, 112, 625).

As might be expected there is a general, although not invariable, parallelism between the susceptibility to produce the oxidised flavour and the  $E_h$  of the milk. De-aeration, bacterial growth which removes oxygen, or addition of anti-oxidants, e.g., ascorbic acid, carotene, or vitamins *A* and *E*, all minimise or prevent the flavour development in milk (Guthrie, Hand, and Sharp, Milk Plant Month. 1939, 28, No. 4, 26), as do appropriate additions of grass or hay (which contain ascorbic acid, carotene, etc.) to the feed of the cow (Brown, Vanlandingham, and Weakley, J. Dairy Sci. 1941, 24, 925). Factory practices which have some preventative effects include de-aeration (Sharp, Hand, and Guthrie, J. Milk. Tech. 1940, 3, 228; Assoc. Bull. Int. Assoc. Milk Dealers, 1942, 34, 365), pasteurisation (Martin, Proc. 30th Ann. Conv. Intern. Assoc. Milk Dealers, 1937, p. 169; J. Dairy Sci. 1938, 21, Abstr., 255), homogenisation (Thurston *et al.*, *ibid.* 1936, 19, 671), and elimination of metallic contamination (copper and iron). The effect of heat treatment is ascribed to the production of sulphhydryl groups in the milk (*see under* “cooked” flavour in section (c) *below*) which lower its  $E_h$  while agitation (homogenisation) has been claimed to be partly effective through the removal of the phosphatide from the surface of the fat globules to the plasma where, being more widely dispersed, it is less

readily oxidisable (according to Thurston *et al.*, *l.c.*).

(ii) *Rancidity* is caused by the hydrolysis of the butterfat by lipase (see p. 108a) and is different from the "oxidised" flavour; indeed lipase has an antioxidant effect, according to Davies (J. Dairy Res. 1932, 3, 254). The butyric flavour which first develops in milk as a result of lipase activity is followed by a "bitterness," often evident in milk drawn late in the lactation period when the lipase content is high (Herrington and Krukowsky, J. Dairy Sci. 1939, 22, 127). Heat treatment (pasteurisation) of milk effectively prevents the development of this flavour (see under "Enzymes," p. 108a), while homogenisation (without pasteurisation) accentuates it because the water-fat interface, the site of the enzyme activity, is thereby increased.

(iii) "*Off*" Flavours of a Considerable Variety, including flavours reminiscent of different roots, may develop in milk owing to the action of various bacteria and yeasts. A bitter flavour may also result from a peptonising action of certain organisms (Orla-Jensen, "Dairy Bacteriology," London, 1931, p. 81).

(c) Flavours due to Processing Treatments of milk include the well-known "cooked" flavour resulting from heat-treatment. This flavour has been ascribed to bodies with sulphhydryl groups, including hydrogen sulphide, formed particularly from the soluble proteins and from the protein associated with the fat globules (Townley and Gould, J. Dairy Sci. 1943, 26, 843, 853). Gould (*l.c.*) gives the following temperatures above which the flavour develops:

Momentary heating . . .	76-78°C.
3-minutes holding period . .	74-76°C.
30 " " . . .	70-72°C.

It is interesting to note that 1 p.p.m. of copper raises the critical temperature by about 6° and increases the  $E_h$  of the milk (Gebhardt and Sommer, J. Dairy Sci. 1931, 14, 416; Ind. Eng. Chem. [Anal.] 1931, 3, 414). A metallic taste in milk, as distinct from induced "oxidised" flavour, may result from contamination by various metals, e.g., addition of more than 2 p.p.m. of copper lactate or more than 20 p.p.m. of ferric lactate (M. Donauer, from T. Mojonner and H. C. Troy, "Technical Control of Dairy Products," Chicago, 1932, p. 858).

## 12. PROCESSING TREATMENTS.

(a) Heat Treatment (Pasteurisation and Sterilisation).—The object of the heat-treatment of milk is to enhance its keeping properties and to render it bacteriologically safe. Limited heat-treatment (pasteurisation), by either of the two methods described below, inactivates all the pathogenic organisms and the majority of other bacterial types, thereby extending the life of the milk with little or no effect on its flavour or nutritive properties. "*Holder*" pasteurisation of milk, officially recognised in Britain in 1936, involves heating to 145-150°F., holding at that temperature for 30 minutes and rapid cooling. Such a procedure, which must be a batch process, gives a bacteriologically satisfactory product. Simplified

of the process by pasteurising in the bottle has been urged repeatedly, but there are attendant difficulties and the method has not received official sanction.

"Flash" or "High Temperature, Short Time" (H.T.S.T.) Pasteurisation requires rapid raising of the temperature of the milk to 162-165°F., which is maintained for 15-30 seconds and followed by rapid cooling. The process is carried out in continuous-flow heaters. This method of heating milk affects its "cream line" (the visible layer of cream which forms on standing), considered a good selling feature. Incidentally, Dahlberg (New York Agric. Exp. Sta. Tech. Bull. No. 203, 1932) stated that to preserve the cream line, heating conditions must not be more severe than heating for 20 seconds at 160°F. H.T.S.T. pasteurisation has a smaller margin of safety than has the "holder" process, and while it is satisfactory for milk with low bacterial count, it is less safe for milk with a high count. Milk pasteurised by the H.T.S.T. process was found by Hileman *et al.* (J. Dairy Sci. 1941, 24, 305) to yield higher bacterial counts on tryptone-glucose-skim milk agar-media at 37° than "holder" process pasteurised milk, a difference ascribed by them to the thermophilic bacteria generally present. The H.T.S.T. method is very popular in the U.S.A., and was officially approved as a provisional measure in Britain in 1941 as an alternative to "holder" pasteurisation.

Sterilisation of milk is not widely used, as the product has only limited acceptance by the public owing to its "cooked" flavour. The process is normally carried out in narrow-necked sealed bottles, which are heated in boiling water for 20-30 minutes. In order to avoid the formation of cream "plugs" in the neck of the bottle, which occurs with ordinary milk, homogenised milk is used.

*The Effect of Heat on the Constituents of Milk.*—The stability of different samples of milk on heating differs. Heat precipitates protein from those in which the salt balance is such that the calcium and magnesium contents are high and the citrate and phosphate contents low; furthermore, increased acidity (e.g., 0.21% calculated as lactic acid) is also a contributory factor (Sommer and Binney, *ibid.* 1923, 6, 176).

At 60-80°C. coagulation of lactalbumin and lactoglobulin occurs, but the casein is little affected. Rowland (J. Dairy Res. 1933-34, 5, 46; 1937, 8, 1) found that the amount of lactalbumin and lactoglobulin denatured depended on the temperature and time of heating. Further, in 30 minutes at 63°C. ("holder" pasteurisation), 10% of the soluble protein was denatured, at 100°C. it was completely denatured in 5-10 minutes, while at 115-120°C. there was also appreciable hydrolysis of protein. The mineral constituents exhibit some change, partial precipitation of buffer salts occurring, e.g., Bell (J. Biol. Chem. 1925, 64, 391) found losses of soluble calcium and phosphate up to 9% of the total present, depending on the temperature of heating, while Lampitt and Bushill (Biochem. J. 1934, 28, 1305) showed that losses of 4% of dialysable calcium and phosphate occur on heating milk for 1 hour at

100°C. Tricalcium phosphate is precipitated on heating milk, particularly on sterilisation.

The titratable acidity of milk increases on heating (pasteurisation), owing to the change in the salt equilibrium. More drastic heating (sterilisation) also causes a greater increase of titratable acidity, resulting from decomposition of lactose (Whittier and Benton, *J. Dairy Sci.* 1927, 10, 126).

Sterilisation causes the colour of milk to become yellower, owing to incipient caramelisation of lactose in presence of protein (Ramsey *et al.*, *ibid.* 1933, 16, 17), but in pasteurised milk this effect is scarcely perceptible. Heating also causes the development of a characteristic odour, due probably to the evolution of ammonia and volatile sulphur compounds.

*Skin on Milk.*—When milk is heated at ca. 60°C. in an open vessel, a skin gradually forms on the surface, owing partly to evaporation of water and partly to surface denaturation of the protein. The fat which rises to the surface during the heating is found in the skin and may amount to 20–60% of its dry-solids content (W. L. Davies, "Chemistry of Milk," London, 1939, p. 351); the skin from homogenised milk contains little fat (Winkler, *Milch. Ztg. Wien.* 1927, 34, 287; *Milch. Forsch.* 1928, 6, Abstr., 57).

(b) *Homogenisation.*—The process of homogenisation of milk is usually carried out in order to minimise the formation of a cream layer by the separation of fat on standing. It is effected by forcing the milk through a fine orifice under high pressure (ca. 2,500 lb. per sq. in.), whereby the fat globules are sub-divided to a more uniform size of 2 $\mu$ . or less. Homogenisation is usually carried out at pasteurisation temperature, at which the effect is optimum (Rahn, *Milch. Forsch.* 1925, 2, 383). The treatment increases the amount of protein adsorbed on the fat globules, owing to an increased fat/water interface at which protein is adsorbed. Wiegner (*Kolloid-Z.* 1914, 15, 105) found increased protein adsorption by reduction of average globule size from 2.9 to 0.27 $\mu$ . by homogenisation. Coalescence of the fat globules is largely prevented in homogenised milk, and consequently, on centrifuging, little fat-separation occurs; homogenised milk cannot be churned. The foaming tendency and viscosity of raw milk are increased by homogenisation, but in the case of pasteurised milk they are decreased (Trout *et al.*, *Tech. Bull. Mich. Agric. Exp. Sta.* 1935, No. 145, p. 3; *Amer. Chem. Abstr.* 1935, 29, 5526).

(c) *Irradiation.*—The fortification of milk with respect to its vitamin-D content to produce antirachitic milk has been much studied in America, where such milk is manufactured in quantity. The milk is exposed to ultra-violet light for a short time (15 seconds) in a thin film to ensure good penetration of the light; long exposure, especially in presence of oxygen, causes the development of undesirable flavour. Maximum vitamin-D (1.6 I.U. per g.) is obtained with an ultra-violet light-energy input of 300 joules per g. of milk (Beck *et al.*, *Ind. Eng. Chem.* 1938, 30, 632; O'Brien *et al.*, *ibid.*, p. 839). Irradiation also has a bactericidal action, but complete sterilisation of milk cannot be effected even after several minutes' exposure, owing to

absorption of light by the proteins present (Ayers and Johnson, *Zentr. Bakt.* 1914, II, 40, 109).

(d) *Concentration.*—In order to improve the keeping properties of milk much more than is possible by pasteurisation, without impairing the flavour to the extent that occurs on sterilisation, milk is concentrated at 130–145°F. under reduced pressure. The concentrated milk, with or without added sugar, is usually known as "condensed" or "evaporated" milk, respectively. The composition of these products is specified in the Public Health (Condensed Milk) Regulations, 1923; the "full-cream" products must contain not less than 9% of fat and not less than 26% of milk solids including fat (not less than 7.8% of fat and not less than 25.5% of milk solids including fat, according to war-time regulations, 1940); condensed skimmed milk must contain not less than 26% and evaporated skimmed milk not less than 20% of milk solids, including fat. The sweetened products usually contain ca. 40% of sucrose.

To obtain satisfactory products it is essential to use milk of high quality from healthy cows and having low bacterial counts. For the final products to conform to legal requirements the original milk is analysed, and if necessary standardised, with respect to fat and total-solids contents.

*Condensed Milk.*—The process entails the following stages:

(i) *Forewarming*, in which the milk is heated at 200–250°F. for a short while. If this process is carried out at 200°F. the final product tends to thicken on storage, but above 212°F. this is minimised. This not only effects sterilisation of the milk and removes carbon dioxide, but also minimises foaming later, and facilitates solution of sucrose added subsequently.

(ii) *Addition of sucrose*, usually 17–18 lb. per 100 lb. of milk.

(iii) *Concentration* in a vacuum pan at 130–145°F. with a vacuum of 24–27 in. of mercury. The conclusion of this stage is determined by a sp.gr. determination.

(iv) *Rapid cooling* to ensure that the lactose crystals which form are small, so giving a product with smooth texture.

(v) *Packing into cans.*

*Evaporated Milk.*—The stages of manufacture are as follows:

(i) *Forewarming* at 200°F. for 5–10 minutes. In addition to the advantages noted above, this stage is of importance because it raises the heat-coagulation temperature in the final sterilisation stage.

(ii) *Concentration* (as with condensed milk, *see above*).

(iii) *Superheating* in the vacuum pan to 180–190°F. in order to increase the viscosity by coagulating part of the lactalbumin, and to prevent fat separation (this stage is not always carried out).

(iv) *Homogenisation*, to prevent fat separation on storage.

(v) *Filling into cans.*

(vi) *Sterilisation*, usually at 243°F. for 15 minutes, followed by rapid cooling to 75°F. Sterilisation causes some caramelisation of



lactose, with consequent darkening of the colour of the product.

(e) **Separation.**—The fat globules of milk, with their adsorbed layer [Section 3 (a)], rise to the surface of the milk on standing (gravity creaming), the larger globules rising more rapidly than the smaller ones. A computation of the rate of rise of the fat globules in milk has been made (Richmond, *op. cit.*, p. 143), but it takes no cognisance of the aggregation of the globules (clumping) which is known to occur, particularly at low temperature. This aggregation is at a minimum at 63–75°C. (creaming power is partially lost on pasteurisation) and maximum at 7–8°C. (Weinlig, *Forsch. Geb. Milchw. Molkerei*, 1922, 2, 127, 175; *Amer. Chem. Abstr.* 1923, 17, 1675; Rahn, *Milch. Forsch.* 1925, 2, 383). Other factors affecting fat clumping include the fat content of the milk, the fat-globule size and the properties of the aqueous phase (see "Churning of Cream," below).

The preparation of cream by gravity creaming of milk is slow and inefficient, as an appreciable proportion of the fat remains in the lower layer. The recovery of practically the whole of the fat as cream is effected by submitting milk, warmed to 29–30°C., to a centrifugal force of *ca.* 1,000 *g.* Rahn (*l.c.*) stated that of the fat globules present in milk, all those above 3 $\mu$ . in diameter and most of those 2–3 $\mu$ . in diameter are found in the cream on mechanical separation.

### 13. CREAM.

The Food and Drugs Act, 1938, defines cream as "that part of milk rich in fat which has been separated by skimming or otherwise." Modern centrifugal separators can be adjusted to yield cream with fat content ranging from 10 to 65%, the normal range being 45–55%, while, for canning, cream is usually prepared with 20–30% of fat. The non-fatty phase of cream is essentially the same in composition as that of the original milk.

The viscosity of cream depends on the size of the fat globules, and to a less extent on the fat content. The normal laws of viscosity do not hold, the consistency being that of a plastic substance rather than that of a liquid.

Homogenisation of cream is usually effected in two stages. The first stage, at a high pressure (up to 5,000 lb. per sq. in.), reduces considerably the size and increases the number of the fat globules, but at the same time the cream becomes a thick plastic mass. The second stage, at a low pressure (up to 1,000 lb. per sq. in.) reduces the viscosity of the product.

Artificial thickening of cream was formerly effected by addition of such substances as gelatin, agar, and viscogen (calcium saccharate), which improve the whipping properties of cream, but the practice is now prohibited by the Preservatives in Foods Regulations, 1927.

Whipping aerates cream to a stable form of cell-like structure, to which, it is believed, denatured protein at the air-liquid interface contributes some of the stability. The ease of whipping and rate of aeration are greater in cream with large fat-globules and with high fat-content, and also when clumping of the globules has occurred, *e.g.*, on holding at a temperature

of *ca.* 40°F. when the fat is in a semi-solid condition. The degree of aeration on whipping cream is limited by the presence of cane sugar, by pasteurisation, and by homogenisation. Continued whipping of cream causes an increase in volume up to a maximum, followed by a reduction in volume when coalescence of the fat globules occurs and butter separates.

**Churning of Cream.**—When cream is agitated (churned), aggregation of fat globules and increase in the size of the fat clumps occur, followed by breaking of the emulsion. The plastic mass of fat (butter) is an emulsion in which fat is the continuous phase, containing dispersed globules of water and air, stabilised by hydrated protein. The ease of churning and the yield of butter are influenced by several factors, such as temperature (usually 13–18°C.), acidity, and fat content of the cream (fat content usually 30–33%), and also size and extent of clumping of the fat globules. Churning is facilitated by slightly increased acidity, but if the acidity is too high, casein is precipitated in the form of clots in the butter.

Two theories have been propounded to explain the formation of butter on churning cream:

- (a) the foam theory (Rahn, *Kolloid-Z.* 1922, 30, 341), according to which a foam is first produced containing fat globules in the aqueous phase; the foam then collapses, when the fat separates as a plastic mass in which water is occluded;
- (b) the phase-inversion theory (Fischer and Hooker, "Fats and Fatty Degeneration," New York, 1917, p. 93; quoted by W. L. Davies, "Chemistry of Milk," London, 1939, p. 273) which postulates the conversion of a fat-in-water emulsion (cream) to a water-in-fat emulsion (butter), protein being the stabiliser in both emulsions. During churning the fat globules coalesce, thereby decreasing the area of the water/fat interface, and when this reaches a critical value the emulsion breaks.

The "feathering" of cream, which occurs on adding it to hot coffee, is largely an acidity effect; the acidity may be that of the cream itself (Webb and Holm, *J. Dairy Sci.* 1928, 11, 243) or that of the coffee. The effect is more evident when the coffee is too concentrated or has been too long infused, and when the cream is added too slowly or in only small amount (Whittaker, *ibid.* 1931, 14, 177). Fresh un-homogenised cream is stated not to "feather," while homogenisation or addition of 0.1% of sodium bicarbonate or phosphate to the cream reduces the tendency (Doan, *Creamery and Milk Plant Month.* 1931, 20, No. 1, 33).

**Clotted Cream** is prepared by allowing cream to rise to the surface of milk and then gradually heating to 180–190°F. and cooling slowly; the clotted cream layer is then removed. The ratio of non-fatty solids to water in clotted cream is much higher than that in ordinary cream and milk, owing to loss of water by evaporation, while the ratio of ash to non-fatty solids is somewhat reduced, owing presumably to deposition of certain of the salts (calcium) during the heating.

Artificial Cream (better known as "reconstituted" cream) is defined in the Food and Drugs Act, 1938, as an "article of food resembling cream and containing no ingredient which is not derived from milk except water." The differentiation of such a product from fresh cream is difficult; Richardson (Analyst, 1928, 53, 334; 1933, 58, 686) suggested two tests which may be applied.

Synthetic Cream is an emulsion prepared from a solution of the non-fatty solids of milk (skimmed milk) and a fat other than butterfat.

#### 14. SEPARATED MILK.

The fat content of milk separated by centrifugal methods is usually 0.05–0.3%, but it will exceed this when the cream is removed by non-mechanical means. The non-fatty solids content is higher than that of the whole milk from which it is prepared, dependent upon the amount of fat removed; the Food and Drugs Act, 1938, specifies that separated milk shall have not less than 8.7% of non-fatty solids. Separated milk, which may be regarded as a by-product from the manufacture of cream from whole milk, is a relatively cheap commodity utilised for a wide variety of manufacturing purposes, including the manufacture of dried separated milk and skimmed-milk cheese.

#### 15. FERMENTED MILKS.

These are prepared in various countries by the action of micro-organisms on milks from different species (for historical survey, see Corninboeuf, Sci. Agric. 1933, 13, 466, 596). The better known are the following:

(a) *Yoghourt*, the product of the action of lactic acid bacteria, especially *L. bulgaricus* and *Str. thermophilus* (Damm, Apoth.-Ztg. 1929, 44, 1127; Amer. Chem. Abstr. 1930, 24, 201), on pasteurised or partly evaporated cows' milk, or sometimes sheep's or buffaloes' milk. Rosell (Canad. Publ. Health J. 1933, 24, 344) recommends incubation with the organisms at 45–48°C. for 23–36 hours, when the lactic acid content may rise to 3.5%.

(b) *Kefir* (sometimes known as "champagne milk"), prepared by the action on cows' milk of kefir grains, which contain torula yeast and bacteria including *Str. lactis* (Damm, l.c.). It is usually made in closed vessels and effervesces when these are opened. The alcohol content is about 1.2%.

(c) *Koumiss*, derived from unpasteurised mares' milk by the action of *L. bulgaricus*, *B. lactis acidii*, and a lactose-fermenting torula (Belokopytowa and Lück-Smirnowa, Zentr. Bakt. 1929, II, 79, 185).

#### 16. MILK OF MAMMALS OTHER THAN THE COW.

The number of recorded analyses of certain of the different milks is strictly limited, and in all cases the composition is probably affected by the factors already mentioned in Section 5. The figures given in Table XV cannot necessarily be regarded as satisfactory averages, as is the case for those of cows' milk (from Table II) inserted for comparison. The milks from different species of mammals differ in their behaviour on treatment with rennet, those from cow, ewe,

buffalo, and goat giving hard curds, whereas those from woman, ass, and mare give no curd, or a very soft curd (Richmond, *op. cit.*, p. 63).

All these different types of milk contain fat dispersed as fine globules, sugar, protein, and mineral matter (including calcium, phosphate, and chloride), but the proportions of the various constituents differ. Furthermore, there are some differences in the composition of certain of the constituents, e.g., the amounts of volatile acids in the fat vary (they are much lower in the fat from human milk than in that from cows' milk), while some doubt has been expressed whether all the sugar in human milk is lactose (see Section 3 (b) (iv)).

#### 17. ANALYSIS OF MILK.

Working details of the various analytical methods are not appropriate to this article (they may be found in Richmond, *op. cit.*, pp. 239 *et seq.*); an outline only is given here of the principles of the methods, together with relevant references. Apart from the bacteriological examination (Section 10), the routine analysis of milk usually involves determination of specific gravity, acidity, and fat and total-solids contents.

(a) *Dirt Content*.—The term "dirt" is applied to extraneous particles found in milk. They include epithelial, pus, and blood cells, leucocytes, particles of dung, hay, straw, vegetable matter, dust, hairs, and fibres. Most of the bacteria in milk should also be included under the general term "dirt," but they are not determined by the methods of analysis usually employed. The method advocated by the Society of Public Analysts and other Analytical Chemists (Analyst, 1937, 62, 287) involves separation of the dirt by sedimentation in a special container for 72 hours, with occasional stirring (preservative is added to the milk), followed by washing of the sediment with ammonia and water and measurement of its volume after centrifuging in a graduated centrifuge tube. The suggested limits (*ibid.*, p. 301) are 1 part by volume of sediment per 100,000 for clean milk, with an upper limit of 2 parts per 100,000, although it must be borne in mind that milk with less than this amount of dirt is not necessarily clean, as no account is taken of bacterial content.

(b) *Specific Gravity* is usually determined by means of a lactometer, which is a hydrometer calibrated to indicate the sp.gr. at 60°F. Tables enable the reading to be corrected when the temperature differs from 60°F.

(c) *Fat Content*.—In order to facilitate the separation of the fat from milk prior to its determination, the protein is usually first brought into solution by either (i) acid treatment, sulphuric acid being used in the Gerber, Babcock, and Leffmann-Beam methods, and hydrochloric acid in the Werner-Schmidt method, or (ii) addition of ammonia, as in the Röse-Gottlieb method. The amount of fat separated is then determined, either by measurement of its volume, as in the three first-named methods, or by weighing, after solvent extraction, as in the other two methods. The Röse-Gottlieb method is advocated by the Milk Pro-



TABLE XV.—COMPOSITION OF MAMMALIAN MILKS.

Species.	No. of samples.	Total solids, %.	Fat, %.	Sugar (lactose), %.	Casein, %.	Other protein, %.	Ash, %.	References.
Mare . .	104	5.33-18.74	0.09-7.88	1.65-8.78	0.55-7.60		0.28-0.95	Linton, J. Agric. Sci. 1931, 21, 669.
Ass . .	(av. —)	10.06	1.50	6.14	2.60	2.10	0.51	Fleischmann - Weigmann, "Lehrbuch der Milchwirtschaft," Carey, 1932, p. 147.*
Mule . .	—	8.50	1.50	4.80	1.61	—	0.35	W. L. Davies, "Chemistry of Milk," London, 1939, p. 7. Barthe, J. Pharm. Chim. 1905, [vii], 21, 386. Richmond, <i>op. cit.</i> , p. 79.
Zebra . .	—	—	4.80	5.39	3.03	—	—	
Camel . .	—	12.39	5.38	3.26	2.95	—	0.70	
Llama . .	—	13.45	3.15	5.60	3.00		0.80	Lythgoe, J. Dairy Sci. 1940, 23, 1097.
Goat . .	335 individual animals	0.12-21.06	1.00-9.80	3.56-5.65	2.30-6.08		0.60-1.20	
American Buffalo	—	13.67	1.60	5.74	4.21	0.51	0.96	Shutt, Analyst, 1932, 57, 451.
Indian Buffalo	231	—	2.0-12.0	4.0-5.3	—	—	—	Ghosh and Datta Roy, Indian Med. Gaz. 1941, 76, 279.
Egyptian Buffalo	61	17.91	7.96	4.86	4.16		0.78	Pappel and Hogan, Publ. No. 4, Hygiene Inst. Egypt Dept. Pub. Health, 1944.*
Reindeer . .	—	36.70	23.46	2.50	10.30		1.44	Barthe and Bergman, Z. Nahr. u. Genussm. 1913, 26, 238.
Ewe . .	—	19.88	7.94	3.74	6.83		0.93	Godden and Puddy, J. Dairy Res. 1935, 6, 307.
Cat . .	3	—	4.49-4.98	4.71-4.80	3.60-3.79	3.11-3.30	0.60	Davies, <i>op. cit.</i> , p. 7.
Blitch . .	—	24.54	9.57	3.00	11.16		0.73	Richmond, <i>op. cit.</i> , p. 79.
Rabbit . .	—	30.50	10.45	1.95	15.51		2.56	Richmond, <i>op. cit.</i> , p. 79.
Gulnea pig	2	—	7.13	2.16	4.70		0.55	Davies, <i>op. cit.</i> , p. 7.
Rat . .	—	31.70	14.80	2.80	9.2		2.0	Davies, <i>op. cit.</i> , p. 7.
Vixen . .	15	18.07	6.30	4.56	6.25		0.96	Young and Grant, J. Biol. Chem. 1931, 93, 805.
Porpoise . .	—	58.80	48.50	1.33	11.10		0.58	Richmond, <i>op. cit.</i> , p. 79.
Whale . .	—	51.33	43.67	—	—		0.46	Richmond, <i>op. cit.</i> , p. 79.
Sow . .	4	—	6.32-9.54	3.10-4.44	3.26-3.76	1.45-1.65	1.0	Davies, <i>op. cit.</i> , p. 7.
Elephant . .	—	32.15	19.57	8.81	3.09		0.65	Richmond, <i>op. cit.</i> , p. 79.
Ape . .	—	11.47	3.50	6.02	1.05	0.40	0.24	Richmond, <i>op. cit.</i> , p. 68.
Woman . .	1,154	12.57	3.76	6.98	1.63		0.21	Gardner and Fox, Practitioner, 1925, 114, 153.
Cow . .	—	12.69	3.07	4.78	2.86	0.56	0.73	Table 11.

\* Taken from Associates of L. A. Roger's "Fundamentals of Dairy Science," New York, 1935, p. 17.

ducts Sub-Committee of the Society of Public Analysts and other Analytical Chemists (*ibid.* 1927, 52, 402), primarily for condensed milk, but it is applicable also to fresh milk.

(d) Total Solids Content.—For most routine purposes this is calculated from the determined sp.gr. and fat content of the milk, there being an established relationship between the three properties (*see* Section 7 (h), p. 106c). Determination may be effected by weighing the residue obtained from a known weight (5 g.) of milk after evaporation and drying in an air oven at 98–100°C. to constant weight (3 hours). Reference should be made to the methods of the Society of Public Analysts and other Analytical Chemists (*ibid.* 1927, 52, 402).

(e) Determination of Added Water.—If the non-fatty solids content ( $x$ ) of a sample of whole milk is less than 8.5%, the presence of added water is inferred, the percentage being approximately  $100(8.5-x)/8.5$ . As confirmation, the freezing-point ( $-Y^{\circ}\text{C.}$ ) of the milk (*see* Section 7 (l), p. 107a) is determined, and if this is

higher than  $-0.53^{\circ}$  the presence of added water is established, the percentage being approximately  $100(0.53-Y)/0.53$ . The presence of added water may also be determined from the refractive index of the serum (*see* Section 7 (g), p. 106c), and sometimes detected by the presence of nitrates; nitrate is absent from milk but may on occasions be present in extraneous water added to milk.

(f) Acidity.—This is determined by titration of the milk with 0.1N. sodium hydroxide solution (usually with phenolphthalein as indicator), and is calculated as the percentage of lactic acid. The acidity of good milk is normally 0.16–0.19%. Milk with acidity greater than ca. 0.26% coagulates on boiling. For determination of true lactic-acid content of milk, *see* Lampitt and Bogod, Chim. et Ind. 1932, 26, 11th Congr. Chim. Ind., p. 777; for citric-acid content, *see* Lampitt and Rooke, Analyst, 1936, 61, 654.

(g) Nitrogenous Constituents.—The total nitrogen content is generally determined by

Kjeldahl's method, using a trace of copper sulphate or selenium as catalyst. The nitrogenous constituents may be separated and determined by Moir's method modified by Rowland (references in Section 3 (ii), p. 101*b*), the principle of the separation being as follows:

- (i) casein is precipitated at its isoelectric point, pH 4.65-4.75, by using acetic acid and sodium acetate buffer;
- (ii) from the filtrate there are precipitated
  - (a) lactalbumin and lactoglobulin, by adjusting the pH to 4.75-4.80 and boiling, and
  - (b) lactoglobulin, by saturation with magnesium sulphate at pH 6.8-7.2;
- (iii) proteose-peptone is precipitated by addition of trichloroacetic acid to a concentration of 8% in the filtrate (F) obtained after removal of casein and lactalbumin+lactoglobulin (effected by heating the milk to 95°C. to coagulate lactalbumin and lactoglobulin, and then precipitating casein by adjustment of the pH to 4.7);
- (iv) non-protein nitrogen is determined in filtrate (F), or on the serum obtained by adding trichloroacetic acid to a concentration of 12% at room temperature and filtering.

In all the above cases, the protein precipitated is calculated from the nitrogen content ( $\times 6.38$ ) of the solution before and after precipitation. While the use of the factor 6.38 is correct for casein, it is a little low for the other milk proteins [from the analyses of lactalbumin and lactoglobulin made by Van Slyke and Bosworth (J. Biol. Chem. 1913, 14, 203) the factor for these two proteins is calculated to be 6.48]. Calculation of the total protein of milk from protein nitrogen  $\times 6.38$  is reasonably accurate, however, as the proportion of casein present is relatively large.

(h) **Sugar Content.**—The reagents most suitable for the defecation of milk prior to determination of sugars are copper sulphate, zinc sulphate and potassium ferrocyanide, and acid mercuric nitrate. Rapid and accurate determination of lactose in milk (and sucrose in condensed milk) may be made by the polarimetric method advocated by the Society of Public Analysts and other Analytical Chemists (Analyst, 1930, 55, 111). Copper reduction methods, such as that of Bertrand, Lane and Eynon, etc., and the iodometric method of Macara (*ibid.* 1924, 49, 2; 1927, 52, 668) are also applicable. In all of these methods it is necessary to correct for the volume occupied in the defecated solution by the milk protein and fat. This correction is discussed in the paper on the polarimetric method mentioned above.

(i) **Ash Content.**—To minimise the loss of the alkali chlorides during the ashing of milk it is necessary to char the milk solids at a low temperature after evaporation and then to ignite in a muffle at a temperature below red heat (550°C.). After the ash has been weighed a determination of alkalinity may be made, and followed, when required, by determinations of calcium, magnesium, phosphorus, sodium, and

potassium by known methods. For determination of calcium and magnesium, recommended methods are described in papers by Lampitt and Bushill (Biochem. J. 1934, 23, 1305; J.S.C.I. 1937, 56, 411). The possible effect of previous neutralisation of milk on its ash content and alkalinity of ash should be borne in mind.

(j) **Phosphorus.**—The total phosphorus content of milk is best determined colorimetrically on the residue obtained after destruction of the organic matter by means of fuming nitric acid, or sulphuric acid and hydrogen peroxide. Inorganic phosphorus is usually determined on the trichloroacetic acid serum of the milk, and the organic phosphorus calculated as the difference between the total and inorganic phosphorus contents (Lampitt and Bushill, Biochem. J. 1933, 27, 711).

(k) **Chloride.**—When milk is reduced to an ash in the determination of chloride the results may be somewhat low on account of volatilisation. Davies (Analyst, 1932, 57, 79) proposed a rapid, accurate method which obviates this difficulty, depending on destruction of the organic matter of the milk by treatment with concentrated nitric acid and potassium permanganate after fixing the chloride by addition of excess silver nitrate.

(l) **Preservatives.**—The Public Health (Preservatives, etc., in Food) Regulations, 1925-1940, prohibit the addition of any preservative to milk or cream. The most popular preservative used formerly was boric acid, which may be detected by the turmeric paper test, and determined by Thomson's method, modified as described in Richmond, *op. cit.*, p. 307, or by the Government Laboratory method (Analyst, 1923, 48, 416), which is more particularly applicable to cream.

Formaldehyde in milk (or cream) may be detected by Hehner's test, *i.e.*, the formation of a violet ring at the junction of the milk and a layer of concentrated sulphuric acid containing a trace of ferric chloride. This is conveniently carried out during the fat determination by the Gerber method.

Salicylic and benzoic acids may be detected by the usual methods after removal of casein by calcium chloride and sodium carbonate (Revis, *ibid.* 1912, 37, 346) or by hydrochloric acid (Hinks, *ibid.* 1913, 38, 555).

Hydrogen peroxide has been used as a preservative for milk; addition of less than 0.1% is not detectable after 24 hours. Hinks proposed an iodometric method for its determination (*ibid.* 1915, 40, 482).

Hypochlorite is used in sterilising milk plant, and may possibly find its way to the milk, in which it may be detected by the method of Wright and Anderson (*ibid.* 1938, 63, 252), based on the detection of chlorate, an invariable constituent of hypochlorite solutions.

Nitrate has been reported as a preservative in milk (Elsdon and Sutcliffe, *ibid.* 1913, 38, 450), but its presence may be due to added water containing nitrates. Qualitatively it may be detected colorimetrically in a mercuric chloride serum of the milk with diphenylamine or brucine (Elsdon and Sutcliffe, *l.c.*; Lerrigo, *ibid.* 1930, 55, 433) or diphenylbenzidine (Monier-Williams,

*ibid.* 1931, 56, 397). Lerrigo (*l.c.*) claims that the diphenylamine method will detect the addition to milk of 5% of water containing 5 p.p.m. of nitrate nitrogen.

(m) Colouring Matter.—According to the provisions of the Food and Drugs Act, 1938, no colouring matter may be added to milk; its presence may partly hide a deficiency of fat or the presence of extraneous water. Annatto was the colour chiefly used (for detection see Association of Official Agricultural Chemists, "Methods of Analysis," 5th ed., p. 279), but sophistication of milk with caramel, coal-tar colours, carotene, saffron, and turmeric has also been reported.

(n) Sour Milk.—The analysis of sour milk is complicated by two factors:

(i) The presence of clots of protein and fat, with the consequent difficulty of obtaining representative samples for analysis. When such samples cannot be obtained after simple whisking of the mixture, separate analyses of the liquid and solid phases must be undertaken.

(ii) Changes which have occurred in the constituents, for which due allowance must be made in the calculation of results.

The method of analysis usually employed is the "maceration process" described by Thorpo (*Analyst*, 1905, 30, 197), and by Richmond and Miller (*ibid.* 1906, 31, 317), in which, in addition to determination of fat and total solids, determinations are made of alcohol, volatile acid, and ammonia, suitable corrections based on the contents of these substances being applied in the calculation of the original total-solids content of the milk. F. J. Macdonald (*ibid.* 1914, 69, 173) suggested an improved procedure, in which the water and volatile substances are separated by distillation with heptane, the fat being recovered from the latter, the alcohol, etc., determined on the aqueous fraction, and the residual non-fatty solids weighed.

J. H. B.  
H. S. R.

**MILK-TREE WAX**, *cow-tree wax*, is obtained from the latex of a forest tree (Vol. II, 119a), *Brosimum galactodendron* (Fam. Moraceæ), known in Venezuela as *palo de vaca*. It is used in manufacturing candles. Gómez (*Anal. Fís. Quím.* 1935, 33, 360; A. 1936, 1166) states that the wax is crystalline and has m.p. 64–65°; the latex contains rubber (3.48%) and  $\alpha$ -myrrin. The Brazilian milk-tree is *Mimusops elata* (Fam. Sapotaceæ).

J. N. G.

**MILLERITE**. Nickel sulphide, NIS, crystallised in the rhombohedral class of the hexagonal system. Usually as very slender or capillary prisms, often in radiating groups, or interwoven like a wad of hair. Hence colloquially called capillary or hair pyrites. Colour pale brass-yellow, often with a greenish tinge, and metallic lustre. When oxidised it may be coated with a film of the green nickel carbonate, *zaratite*.  $\rho$  5.5, hardness 3–3½. Generally occurs as a low-temperature mineral as tufts in cavities in limestone, dolomite, serpentine, etc., and as an alteration product of other nickel minerals. Also found in meteorites. The mineral is scarce, even though recorded from numerous localities.

D. W.

**MILLON'S REAGENT** is usually prepared by dissolving mercury in an excess of concentrated nitric acid and diluting the solution with water. Millon (*Compt. rend.* 1849, 28, 40) found that the reagent, when added to an albumin solution, gave a white precipitate turning brick-red on boiling. A coloration is observed at a dilution of albumin of 1:100,000. The reaction is given by proteins, provided that they contain the tyrosine group; with gelatin, which does not contain this group, only a faint coloration is obtained. Tyrosine itself and many other substances containing a hydroxyphenyl group give a positive reaction. In characteristic Millon tests the red coloration develops only on heating, but the reaction is not readily specified since a variety of colours is given by the monohydric and dihydric phenols (Chapin, *J. Ind. Eng. Chem.* 1920, 12, 771).

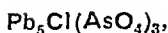
Although the reagent is not specific, it has several applications in analysis. It serves as a stain for protoplasm in botanical sections and for natural silk fibres in admixture with cellulose silk. Several authors have described colorimetric methods based on the use of Millon's reagent (F. D. and C. T. Snell, "Colorimetric Methods of Analysis," 2nd ed., London, 1937, Vol. II, p. 365). Weiss (*Biochem. Z.* 1919, 97, 170) found that the essential components of the reagent are a mercuric salt and nitrous acid. In a colorimetric determination of tyrosine he employed a 10% solution of mercuric sulphate in 5% sulphuric acid; 2 ml. of this solution were mixed with 3 ml. of the sample, and a few drops of a 0.5% solution of sodium nitrite added. Edwards *et al.* (*Analyst*, 1937, 62, 178) determined *p*-hydroxybenzoic and salicylic acids in food. Their reagent was prepared by dissolving mercury in twice its weight of concentrated nitric acid and diluting the solution with twice its volume of water (conveniently recorded as 1:2:2v). When freshly prepared it gave a visible reaction with 0.1 mg. of either of the organic acids in 20 ml. of solution. Fürth and Scholl (*Biochem. Z.* 1931, 243, 274) used a 1:2:2v reagent in the estimation of phenols in urine. Koks (*Pharm. Weekblad*, 1931, 68, 557) made a comparative study of two reagents, (K) of composition 1:1:1v and (S) of composition 1:1:1.7v. (K) was more sensitive, indicating tyrosine at 1:100,000, whereas (S) did not give a coloration at 1:80,000. The formula (K) is prescribed by B.P.C. 1934 and Extra Pharm., 22nd ed., London, 1943, Vol. II, p. 641. R. H. A. Plimmer ("Organic and Biochemistry," 6th ed. London, 1938) adopts the formula 1:2:2v. (See also P. B. Hawk and O. Borgeim, "Practical Physiological Chemistry," 11th ed., London, 1938.)

J. N. G.

**MILORI GREEN**. A light-green pigment in which freshly prepared barium sulphate serves as a support on which lead chromate and Paris Blue (Vol. III, 473c) are precipitated; alternatively, the blue may be incorporated mechanically (F. M. Rowo, "Colour Index," Bradford, 1924, No. 1298; G. Schultz, "Farbstofftabellen," 7th ed., 1931, Vol. I, No. 1454).

J. N. G.

**MIMETITE.** Lead chloroarsenate,



crystallised in the hexagonal system, sometimes as well-developed hexagonal prisms, but generally in rounded globular forms and mammillary crusts closely resembling those of pyromorphite. Colour pale yellow, orange, brown, sometimes colourless, with resinous lustre.  $\rho$  7.0–7.2, hardness 3½. The name *campylite* is given to the yellowish-brown barrel-shaped crystals, formerly abundant at Dry Gill in Cumberland. In the variety *endlicheite*, intermediate between mimetite and vanadinite, the proportion of  $\text{As}_2\text{O}_5$  to  $\text{V}_2\text{O}_5$  is nearly 1:1. Mimetite is an uncommon mineral of secondary origin, found in the near-surface oxidised zone of lead deposits.

D. W.

**MIMOSA.** *Clayton Yellow. Cotton Yellow.*

A fugitive dyestuff for cotton prepared by diazotising primuline and adding ammonia. It yields an indicator paper reddened by caustic alkalis, but not affected by ammonia, alkali carbonates, or phenolates (G. Schultz, "Farbstofftabellen," 7th ed., Vol. I, Berlin, 1929).

J. N. G.

**MIMOSA BARK.** *Wattle bark. Acacia bark.* The mimosas of chief importance for the supply of bark and extract to the tanning industry are trees indigenous to Australia but also grown in plantations in Natal. The trees are known as wattles (*v. ACACIA BARK*, Vol. I, 11c) and are classified as acacia species (sub-order *Mimosae*, Fam. Leguminosae). Mimosa tannin (*v. Vol. VII*, 267b) gives, but not without exception, the reactions of a catechol tannin and is not hydrolysed by tannase (*v. Vol. V*, 425c). For its qualitative reactions, see M. Nierenstein, "Allen's Commercial Organic Analysis," 5th ed., London, 1927, Vol. V; Rudnitzkii, Amer. Chem. Abstr. 1934, 28, 7581; Pollak and Springer, Collegium, 1927, 46.

Several attempts have been made to ascertain the structure of mimosa tannin. Petrie (Biochem. J. 1924, 18, 957) concluded that the tannin of flowers of *mimosae* is a condensation product of phloroglucin, protocatechuic acid, and gallic acid. Douglas and Humphreys (J. Soc. Leather Trades' Chem. 1937, 21, 378) separated mimosa tannin from bark extract by electrodialysis, and estimated its mean molecular weight by a cryoscopic method to be not less than 1,800. This number corresponds to the condensation of at least six catechin molecules (*v. Vol. II*, 433d). Russell and Clark (J. Amer. Chem. Soc. 1939, 61, 2651) synthesised bis-(6:3':4'-trihydroxy)-flavopinacol, a light-red amorphous powder, indistinguishable in its properties from mimosa tannin. Page (B., 1933, 358) discusses the nature of the linkage of mimosa tannin with collagen. This author (J. Soc. Leather Trades' Chem. 1942, 26, 71) finds a close relation between the molecular size of the tannin and the composition of the gelatin-tannin precipitate, and infers the existence in the solution of two mimosa tannins differing in molecular weight by about 260. There is a considerable literature recording the percentage of tannin in mimosa bark. Coombs (*ibid.* 1933,

17, 90) found the following percentage of tannin in commercial barks: *A. decurrens*, green wattle, 42.0; *A. mollissima*, black wattle, 44.0; *A. arundelliana*, 36.6; *A. filicifolia*, 29.0; *A. irrorata*, 28.0; *A. dealbata*, silver wattle, 26.2; *A. pycnantha*, golden wattle, 36.9. (See also Coombs *et al.*, Proc. Roy. Soc. New South Wales, 1923, 57, 313; 1926, 60, 360; 1931, 65, 207; Anon., Bull. Imp. Inst. 1932, 30, 440.) The bark extract is exported from Durban in considerable quantities. The solid extract contains about 63% of tans and 16% of non-tans, the corresponding values of the liquid extract being 30% and 7% (H. Gnamm, "Gerbstoffe und Gerbmittel," 2nd ed., Stuttgart, 1933). Coombs (*l.c.* 1933) has described the working of a bark-extraction plant. For tanning white leather, Woodhead (Amer. Chem. Abstr. 1942, 36, 5667) bleached a wattle extract with sodium "hydrosulphite" ( $\text{Na}_2\text{S}_2\text{O}_4$ ). Varying the pH of a mimosa tanning-liquor revealed two maxima of fixation on hide powder at pH 2–3 and pH 7–8 (Alcjo *et al.*, Amer. Chem. Abstr. 1942, 36, 1801). For grading and sampling the bark, see Taylor, J. South African Forestry Assoc. 1942, No. 8, 103. For methods of analysis, see "Official Methods of Analysis," International Society of Leather Trades' Chemists, A. Harvey, London, 1938. For the industry of wattle bark and extract, see C. O. Williams, Union of South Africa Dept. Agric. Science Bull. No. 63, 1928; No. 74, 1930; No. 106, 1932.

J. N. G.

**MIMOSINE.** An irritant substance extracted from the leaves of the sensitive plant *Mimosa pudica* and of other *mimosae*. According to Soltys and Umrath (Biochem. Z. 1936, 284, 247) the purified extract of *Neptunia plena* causes the leaf movement at a dilution of 1:10<sup>6</sup>. For preparation, see Hesse, *ibid.* 1939, 303, 152. Adams *et al.* (J. Amer. Chem. Soc. 1945, 67, 89) consider that mimosine may be the optically active form of *leucenol* (Maseré, Amer. Chem. Abs. 1937, 31, 4369) and that its constitution may be  $\beta$ -N-(3-hydroxy-6-pyridone)- $\alpha$ -aminopropionic acid or  $\beta$ -(3-hydroxy-6-pyridoxy)- $\alpha$ -aminopropionic acid.

J. N. G.

**MINASRAGRITE.** A highly hydrous sulphate of vanadium,  $\text{V}_2\text{O}_5 \cdot 3\text{SO}_3 \cdot 16\text{H}_2\text{O}$ , crystallising in the monoclinic system. It commonly occurs in granular aggregates, and as a vivid blue encrustation on the vanadium sulphide, *patronite*, at the famous vanadium mine at Minasragra, near Cerro de Pasco in Peru. Museum specimens of *patronite* often become coated with a blue efflorescence of minasragrite, which is itself a valuable source of vanadium.

D. W.

**MINERAL BLUE.** There are numerous synonyms: (a) *Azurite (q.v.)*, Mountain Blue, is native basic cupric carbonate; (b) *Artificial Mineral Blue*, also *Bremen Blue* (*v. Vol. II*, 25c) (J.S.C.I. 1924, 43, 391b), is precipitated cupric hydroxide containing a small amount of basic carbonate; (c) *Prussian Blue* (*v. Vol. III*, 472c, d) and a variety marketed as *Antwerp Blue* (*v. Vol. II*, 25c; see also F. M. Rowe, "Colour Index," Bradford, 1924, No. 1288).

J. N. G.

**MINERAL CAOUTCHOUC.** *Mineral rubber. Elastic bitumen. Elaterite.* A dark-brown, flexible, and elastic mineral found widely distributed in small amounts, e.g., at Castleton, Derbyshire. Geologically it represents a late stage in the alteration of petroleum. The term mineral rubber has also been applied to an insulating material manufactured by blowing air through heated asphaltic petroleum.

J. N. G.

**MINERAL COTTON.** *Mineral Wool. Silicate Cotton. Slag Wool.* A mass of interlaced fibres (diameter ca. 3–15 $\mu$ .) resembling spun glass, obtained by blowing steam or air through melted blast-furnace slag or melted rock. It is used as a heat-insulating lagging for steam pipes, and for lining walls and floors (Theocnen, "Mineral Wool," U.S. Bur. Mines, Information Circ. No. 6984r, 1939).

J. N. G.

**MINERAL GREEN.** Originally the ground mineral malachite (Vol. III, 355d); the term may include other inorganic green pigments, e.g., Scheele's Green (Vol. I, 477d), Schweinfurt Green (*ibid.*, p. 478a), and Chrome Greens (Vol. III, 112d).

J. N. G.

**MINERAL PURPLES.** *Indian Red.* A class of pigments varying in shade from blue-black to brown and containing a high proportion of ferric oxide. Purple of Cassius (Vol. VI, 122b), however, has been termed Mineral Purple.

J. N. G.

**MINERAL WATERS** (v. Vol. I, 155c).

**MINERALOGY.** For more detailed descriptions of minerals than is possible in this Dictionary, the reader should consult such standard works of reference as the following: E. S. Dana, "A Textbook of Mineralogy," 4th ed., by W. E. Ford, New York and London, 1932; C. S. Hurlbut, jun., "Dana's Manual of Mineralogy," 15th ed., New York, 1941; C. Palache, H. Berman, and C. Frondel, "Dana's System of Mineralogy," 7th ed., Vol. I, New York, 1944 [this contains the most authoritative descriptions of the elements, sulphides, thio-salts, and oxides, together with many references. Vol. II (Halides, carbonates, sulphates, borates, phosphates, arsenates, etc.), and Vol. III (Silica, silicates) are in course of preparation]. An elementary text-book is by H. H. Read, "Rutley's Elements of Mineralogy," 23rd ed., London, 1936. A. N. Winchell, "Elements of Optical Mineralogy," 3rd ed., Pt. II, Description of Minerals, New York, 1933, contains optical and other data for a wide range of minerals. "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, New York, 1937, deals comprehensively with non-metallies other than fuels, mainly from the commercial standpoint. The two outstanding journals in the English language are "The American Mineralogist" (issued every two months; Menasha, Wisconsin) and "The Mineralogical Magazine" (London) (a separately paged publication, "Mineralogical Abstracts" gives complete world references to all kinds of mineralogical publications, and is an invaluable guide to the latest works).

For statistics of mineral production, see "The

Mineral Industry of the British Empire and Foreign Countries, Statistical Summary," Imperial Institute, London; "Minerals Yearbook," United States Bureau of Mines, Washington; and "Mineral Industry," New York, McGraw-Hill Book Co., Inc. These works are normally issued annually.

D. W.

## MINERALS AND X-RAY ANALYSIS.

The constituent atoms of nearly all minerals are regularly arranged in continuous three-dimensional patterns. Crystallographers have long regarded this as the only explanation of the regular forms of crystals, the constancy of interfacial angles, and the law of rational intercepts. It led them not only to the description of 32 crystal classes or point-groups based on seven systems of symmetry, but also to the correct derivation of 14 space-lattices and 230 space-groups. The convincing proof that a crystal behaves as a three-dimensional grating to X-rays, and scatters the incident beam in definite directions, related only to the spacings of atomic planes in the crystal and to the wave-length of the radiation, was obtained by a group of physicists at Munich in 1912. Then began the investigation of crystal structures of simple inorganic substances, including minerals, and eventually the unravelling of more complex structures possessed, e.g., by the silicates (W. L. Bragg, "Atomic Structure of Minerals," Oxford, 1937).

The most complete description of crystal structures of inorganic crystals, alloys, and organic compounds is to be found in the "Strukturbericht," which was published as a separately-paged supplement to the Zeitschrift für Kristallographie in four volumes; volume 1 (1931) includes crystal structures published in the period 1913–28, volume 2 (1937) those published in 1928–32, volume 3 (1937) those for 1933–35, and volume 4 (1938) those published during the year 1936. The four volumes include a carefully edited summary of the extensive literature on the subject. Each structure type is described and figured; unit-cell dimensions, unit-cell contents, space-groups, and atomic parameters are given, together with relevant physical data. Tables of crystal-structure data have been published elsewhere, notably by R. W. G. Wyckoff, who does not, however, give separate tables for minerals, but includes them with other inorganic substances ("The Structure of Crystals," 2nd ed., New York, 1931, and supplement to the 2nd ed., 1935, for the years 1930–34). Over 500 cubic elements and compounds have been arranged in order of length of the edge of the unit cube by I. E. Knaggs and B. Karlik, "Tables of Cubic Crystal Structure of Elements and Compounds, with a Section on Alloys by C. F. Elam," London, 1932. These are of value for the X-ray determination of cubic minerals, the crystal structures of which were discovered prior to 1931.

The following Tables have been compiled from the literature\* to give an alphabetical list of crystal structures which have been worked out completely, and of well-known ones for which X-ray data extend only to unit-cell dimensions,

Up to the end of 1940.

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Acmite	$4[\text{NaFeSi}_2\text{O}_6]$ Monoclinic ( $2/m$ )	9.71 8.89 5.26 73° 11'	3.01 2.55 2.92 2.48	Diopside ( $S41$ ) $C2/c$	S.B. 2-130 M.A. 5-186
Actinolite	$2[\text{Ca}_2(\text{Mg}, \text{Fe})_2\text{Si}_8\text{O}_{22}(\text{OH})_2]$ Monoclinic ( $2/m$ )	9.80 17.90 5.27 73° 58'	8.39 3.21 3.42 3.10	Trenolite ( $S42$ ) $C2/m$	S.B. 2-131 M.A. 4-278
Adamite	$4[\text{Zn}(\text{ZnOH})\text{AsO}_4]$ Orthorhombic ( $mmm$ )	8.31 8.51 6.06	5.98 4.25 4.92 3.78	Andalusite ( $S2$ ) $Pnm$	S.B. 2-110 M.A. 7-90
Alabandite	$4[\text{MnS}]$ Cubic ( $m\bar{3}m$ )	5.24	2.61 1.51 1.85 1.17	Rocksalt ( $B1$ ) $Fm\bar{3}m$	S.B. 1-72 M.A. 6-169
Albite	$4[\text{NaAlSi}_3\text{O}_8]$ Anorthic ( $\bar{1}$ )	8.14 12.86 7.17 94° 3' 116° 29' 88° 9'	4.19 3.29 3.63 3.03	Albite ( $S08$ ) $P\bar{1}$	S.B. 3-164, 551 M.A. 6-177
Almandine	$8[\text{Fe}_3\text{Al}_2\text{Si}_5\text{O}_{12}]$ Cubic ( $m\bar{3}m$ )	11.49	2.89 2.36 2.59 2.26	Garnet ( $S14$ ) $Ia\bar{3}d$	S.B. 1-363, 3-150 M.A. 3-433
Alstonite	$2[\text{CaBaC}_2\text{O}_6]$ Orthorhombic	8.77 4.99 6.11		Not determined	M.A. 4-365
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ Rhombohedral ( $3m$ )				
Amalgam	$4[\text{Ag}, \text{Hg}]$ (up to 50% Hg) Cubic ( $m\bar{3}m$ )	7.04 59° 13'	4.90 1.90 2.99 1.74	Not determined $R\bar{3}m$	M.A. 7-87
Amblygonite	$2[\text{Li}, \text{Na}]\text{AlPO}_4(\text{F}, \text{OH})$ Anorthic ( $\bar{1}$ )	4.92 7.05 4.93 107° 22' 97° 27' 109° 50'		Copper ( $A1$ ) $Fm\bar{3}m$	S.B. 1-13 M.A. 8-5
Analcime	$16[\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}]$ Cubic ( $m\bar{3}m$ )	13.68		Not determined $P\bar{1}$	M.A. 8-11
Anatase	$8[\text{TiO}_2]$ Tetragonal ( $4/mmm$ )	5.37 9.54	5.60 2.92 3.43 2.78	Analcime ( $S61$ ) $Ia\bar{3}d$	S.B. 2-148 M.A. 4-369
Andalusite	$4[\text{Al}_2\text{SiO}_5]$ Orthorhombic ( $mmm$ )	7.76 7.90 5.56	3.45 1.65 1.87 1.47	Anatase ( $C5$ ) $I4/amd$	S.B. 1-158 M.A. 3-345
Andesine	$4[(\text{Na}, \text{Ca})\text{Al}(\text{Si}, \text{Al})_3\text{O}_8]$ Anorthic ( $\bar{1}$ )	8.14 12.86 7.17 93° 23' 116° 28' 89° 59'	5.70 3.98 4.60 3.54	Andalusite ( $S2$ ) $Pnm$	S.B. 2-110 M.A. 4-160
				Albite ( $S63$ ) $P\bar{1}$	S.B. 3-164, 551 M.A. 6-177

Andradite	$8[\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}]$ Cubic ( $m\bar{3}m$ )	12.04	2.46 1.01	1.66 1.32	Garnet ( $S14$ ) $Ia\bar{3}d$	S.B. 1-363, 3-150 M.A. 3-433
Anglesite	$4[\text{PbSO}_4]$ Orthorhombic ( $mmm$ )	8.45 5.38	4.21 2.07	2.00 2.01	Barytes ( $I12$ ) $Pnma$	S.B. 1-343 M.A. 3-345
Anhydrite	$4[\text{CaSO}_4]$ Orthorhombic ( $mmm$ )	6.20 6.94	3.49 2.32	2.85 2.20	Anhydrite ( $I11$ ) $Cmcm$	S.S. 1-340 M.A. 3-344
Anorthite	$8[\text{CaAl}_2\text{Si}_2\text{O}_8]$ Anorthic ( $\bar{1}$ )	8.21 12.05 14.16	4.03 2.05	3.18 2.50	Albite ( $S08$ ) $P1$	S.B. 3-164, 551 M.A. 6-177
Anthophyllite	$4[\text{Mg}_2\text{Si}_2\text{O}_7(\text{OH})_2]$ Orthorhombic ( $mmm$ )	18.5 17.9	8.21 3.04	3.24 2.54	Anthophyllite ( $S14$ ) $Pnma$	S.B. 2-137 M.A. 4-403
Antimony	2Sb Rhombohedral ( $\bar{3}m$ )	4.50	3.07 2.13	2.23 1.76	Arsenic ( $I17$ ) $R\bar{3}m$	S.B. 1-25 M.A. 1-193
Apatite	$2[\text{CaF}, \text{Ca}_4(\text{PO}_4)_3]$ Hexagonal ( $6/m$ )	9.37	3.44 2.81	3.10 1.94	Apatite ( $I157$ ) $C6_3/m$	S.B. 2-99 M.A. 8-11
Apophyllite	$2[\text{KF}, \text{Ca}_4\text{Si}_4\text{O}_{20}, 8\text{H}_2\text{O}]$ Tetragonal ( $4/m$ )	9.00	7.75 2.97	3.94 2.50	Apophyllite ( $S62$ ) $P4/mmc$	S.B. 2-145 M.A. 5-29
Aragonite	$4[\text{CaCO}_3]$ Orthorhombic ( $mmm$ )	4.04 7.94	3.38 2.35	2.71 1.99	Aragonite ( $G2$ ) $Pmm$	S.B. 1-295 M.A. 3-22
Arsenic	2As Rhombohedral ( $\bar{3}m$ )	4.14	2.74 1.87	2.04 1.76	Arsenic ( $I17$ ) $R\bar{3}m$	S.B. 1-25 M.A. 3-423
Arsenolite	$4[\text{As}_2\text{O}_5]$ Cubic ( $m\bar{3}m$ )	11.00	6.30 2.75	3.18 2.53	Sennarionite ( $D61$ ) $Fd\bar{3}m$	S.B. 1-245 M.A. 2-107
Atopite	$8[(\text{Ca}, \text{Mn}, \text{Na})\text{Si}_2(\text{O}, \text{OH}, \text{F})_7]$ Cubic ( $m\bar{3}m$ )	10.27			Atopite ( $D62$ ) $Fd\bar{3}m$	S.B. 3-54 M.A. 5-322
Augite	$4[(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6]$ Monoclinic ( $2/m$ )	9.71 5.89	2.93 1.62	2.50 1.42	Diopside ( $S41$ ) $C2/c$	S.R. 2-130 M.A. 5-186
Axinite	$2[\text{Ca}_2\text{MgHAl}_2\text{B}(\text{SiO}_3)_4]$ Anorthic ( $\bar{1}$ )	7.151 9.184 8.935	3.45 2.79	3.13 2.11	Not determined	M.A. 7-163
Baddeleyite	$4[\text{ZrO}_2]$ Monoclinic ( $2/m$ )	5.21 5.26	3.19 2.63	2.85 1.91	Baddeleyite ( $C43$ ) $P2_1/c$	S.R. 4-9 M.A. 6-410

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Barytes	$4[\text{BaSO}_4]$ Orthorhombic ( <i>mmm</i> )	8.85 5.44	3.44 2.72	Barytes ( <i>Jf2</i> ) <i>Pnma</i>	S.B. 1-343 M.A. 3-345
Bastnaesite	$6[(\text{Ca}, \text{La}, \text{D})\text{FCO}_3]$ Hexagonal ( <i>6mm</i> )	7.00	3.50 2.04	Bastnaesite ( <i>771</i> ) <i>Ihce2</i>	S.B. 2-75 M.A. 5-20
Benitoite	$2[\text{BaTiSi}_5\text{O}_{13}]$ Hexagonal ( <i>6m2</i> )	0.00		Benitoite ( <i>532</i> ) <i>C6c2</i>	S.B. 2-123 M.A. 4-270
Borborite	$4[\text{FeSb}_2\text{S}_3]$ Orthorhombic ( <i>mmm</i> )	11.44 14.12	3.02 2.83	Borborite ( <i>133</i> ) <i>Pnam</i>	S.B. 4-35 M.A. 0-410
Bortrandite	$4[\text{H}_2\text{Bo}_2\text{Si}_2\text{O}_5]$ Orthorhombic ( <i>mm</i> )	15.10 8.07		Bortrandite ( <i>546</i> ) <i>Cmc</i>	S.B. 2-141 M.A. 5-324
Beryl	$2[\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}]$ Hexagonal ( <i>6/mmm</i> )	0.21	8.10 4.07	Beryl ( <i>731</i> ) <i>C6/mmc</i>	S.B. 1-305 M.A. 3-343
Garzeite	$8[(\text{Ca}, \text{Na})_2\text{Mg}_2(\text{AsO}_4)_2]$ Cubic ( <i>m3m</i> )	12.35	3.08 2.51	Garzeite ( <i>514</i> ) <i>Ia3d</i>	S.B. 1-303, 3-150 M.A. 0-183
Blindheimite	$8[\text{Pb}_2\text{Sb}_2\text{O}_7]$ Cubic ( <i>m3m</i> )	10.44	2.05 1.56	Andromy Tetroxide ( <i>D02</i> ) <i>Fd3m</i>	S.B. 3-54 M.A. 5-201
Blende	$2[\text{K}(\text{Mg}, \text{Fe})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH}, \text{F})_2]$ Monoclinic ( <i>m</i> )	5.3 9.2	10.0 2.04	Hendricks ( <i>1033</i> ) <i>Cm</i>	M.A. 7-400
Bismutite	$2[\text{BiOCl}]$ Tetragonal ( <i>4/mmm</i> )	3.88	3.45 2.45	Leadfluorohalide ( <i>B1</i> ) <i>P4/mmm</i>	S.B. 2-15 M.A. 8-215
Blamuth	$2\text{Bi}$ Rhombohedral ( <i>3m</i> )	4.74	3.21 1.48	Arsenite ( <i>17</i> ) <i>R3m</i>	S.B. 1-25 M.A. 3-335
Blamuthinite	$4[\text{Bi}_2\text{S}_3]$ Orthorhombic ( <i>mmm</i> )	11.13 11.27	3.80 3.05	Sillinito ( <i>D58</i> ) <i>Pnma</i>	S.B. 3-40 M.A. 5-405
Bixbyite	$16[(\text{Mn}, \text{Fe})_2\text{O}_3]$ Cubic ( <i>m3</i> )	0.37	2.71 1.41	$\text{Mn}_2\text{O}_3$ ( <i>D53</i> ) <i>Ia3</i>	S.B. 2-38 M.A. 4-304
Blende	$4[\text{ZnS}]$ Cubic ( <i>32m</i> )	5.40	3.12 1.03	Ilendite ( <i>D8</i> ) <i>P43m</i>	S.B. 1-70 M.A. 7-385
Bochmitite	$4[\text{AlOOH}]$ Orthorhombic ( <i>mmm</i> )	3.78 11.8	0.21 2.98	Tephrochalcite ( <i>E4</i> ) <i>Pnam</i>	S.B. 3-06 M.A. 0-111



Boracite	$8[\text{Cl}_2\text{Mg}_6\text{B}_4\text{O}_{26}]$ Orthorhombic ( <i>nmm</i> )	17-07 17-07	12-07	5-00 3-01	3-50 2-70	Uncertain <i>Cmc</i>	M.A. 6-46 S.B. 3-511
Borax	$4[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$ Monoclinic ( <i>2/m</i> )	11-82 10-61	12-30 73° 25'	5-77 2-82	4-86 2-56	Not determined <i>C2/c</i>	M.A. 6-335
Bornite	$8[\text{Cu}_5\text{FeS}_4]$ Cubic ( <i>m3m</i> )	10-93		3-31 2-74	3-15 1-94	Uncertain <i>Fd3m</i>	M.A. 7-82
Boulangerite	$8[\text{Pb}_5\text{Sb}_4\text{S}_{11}]$ Monoclinic ( <i>2/m</i> )	21-52 23-16	8-07 70° 12'	3-07 2-33	2-77 1-85	Not determined <i>P2<sub>1</sub>/a</i>	M.A. 8-7
Bournonite	$4[\text{CuPbSbS}_3]$ Orthorhombic ( <i>mmm</i> )	8-10 8-05	7-75	3-82 2-56	2-72 1-76	Not determined <i>Pmm</i>	M.A. 5-175
Braunite	$16[3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_4]$ Tetragonal ( <i>4/mmm</i> )	13-28	18-58	2-09 1-05	2-14 1-12	Not determined <i>I1/acd</i>	M.A. 7-354
Breithauptite	$2\text{NiSb}$ Hexagonal ( <i>6/mmm</i> )	3-92	5-11	2-85 1-97	2-05 1-62	Niecolite ( <i>B8</i> ) <i>C6/mmc</i>	S.B. 1-84 M.A. 3-19
Brochantite	$4[\text{Cu}_4(\text{SO}_4)(\text{OH})_6]$ Monoclinic ( <i>2/m</i> )	13-05 9-82	5-85 76° 35'	0-20 2-05	3-33 2-19	Not determined <i>P2<sub>1</sub>/a</i>	M.A. 7-193
Bromellite	$2[\text{BeO}]$ Hexagonal ( <i>6mm</i> )	2-60	4-37	2-34 2-06	2-19 1-35	Wurtzite ( <i>B1</i> ) <i>C6mc</i>	S.B. 1-78 M.A. 3-5
Brookite	$8[\text{TiO}_2]$ Orthorhombic ( <i>mmm</i> )	9-17 5-44	5-14	3-22 1-69	2-46 1-36	Brookite ( <i>C21</i> ) <i>P6ca</i>	S.B. 2-14 M.A. 4-23
Brucite	$\text{Mg}(\text{OH})_2$ Hexagonal ( <i>3m</i> )	3-12	4-73	4-75 1-70	2-35 1-57	Cadmium Iodide ( <i>C6</i> ) <i>C3m</i>	S.B. 1-161 M.A. 6-411
Brushite	$8[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$ Monoclinic ( <i>2</i> )	10-3 15-1	6-1 84° 53'	7-60 3-01	4-24 2-62	Related to Gypsum <i>C<sub>2</sub></i>	M.A. 7-89
Calaverite	$2[\text{AuTe}_2]$ Monoclinic ( <i>2/m</i> )	7-18 4-16	5-07 90° ± 30'	2-99 1-77	2-09 1-68	Not determined <i>C2/m</i>	M.A. 6-170
Calcite	$2[\text{CaCO}_3]$ Rhombohedral ( <i>3m</i> )	6-35	10° 7'	3-01 1-92	2-28 1-57	Calcite ( <i>G1</i> ) <i>R3c</i>	S.B. 1-292 M.A. 6-192
Calclonite	$2[\text{Cu}_2\text{Pb}_2(\text{SO}_4)_3(\text{CO}_3)(\text{OH})_2]$ Orthorhombic ( <i>mmm</i> )	7-11 20-06	6-55			Not determined <i>Pmm</i>	M.A. 7-165
Calomel	$4[\text{HgCl}]$ Tetragonal ( <i>4/mmm</i> )	4-17	10-89	1-16 2-03	3-17 1-97	Calomel ( <i>D31</i> ) <i>I4/mmm</i>	S.B. 1-237 M.A. 3-127

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Cancrinite	$3(\text{Na}_2\text{Al}_2\text{O}_4 \cdot \text{Si}_2\text{O}_4) \cdot 2(\text{CaCO}_3 \cdot \text{H}_2\text{O})$ Hexagonal (6)	12.72      5.18		Cancrinite (S33) $C6_3$	S.B. 3-150 M.A. 5-325
Carnallite	$12[\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}]$ Orthorhombic ( $mmm$ )	9.54      22.52 16.02		Uncertain $Pban$	M.A. 7-490
Cassiterite	$2[\text{SnO}_2]$ Tetragonal (4/ $mmm$ )	4.72      3.17	3.33      2.63 2.36      1.76	Rutile (O4) $P4/mmm$	S.B. 1-155 M.A. 3-345
Celestine	$4[\text{SrSO}_4]$ Orthorhombic ( $mmm$ )	8.36      6.84 5.36	3.29      2.97 2.70      2.03	Barytes (P2) $Pnma$	S.B. 1-343 M.A. 3-345
Celsian	$4[\text{BaAl}_2\text{Si}_2\text{O}_8]$ Monoclinic (2/ $m$ )	8.13      7.20 13.10      64°		Sanidine (S67) $C2/m$	S.B. 3-161 M.A. 6-177
Cerussite	$4[\text{PbCO}_3]$ Orthorhombic ( $mmm$ )	5.17      6.13 8.48	3.56      2.47 2.07      1.83	Aragonite (G02) $Pnma$	S.B. 3-84 M.A. 7-391
Chabazite	$2[\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}]$ Rhombohedral ( $\bar{3}m$ )	9.16      94° 24'	9.80      4.80 4.35      2.93	Chabazite (S34) $R\bar{3}m$	S.B. 3-151 M.A. 5-162
Chalcocite	$160[\text{Cu}_2\text{S}]$ Orthorhombic	11.8      22.7 27.2	2.40      1.99 1.89      1.72	Not determined	M.A. 5-175
Chalcantithite	$2[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ Anorthic (1)	6.12      82° 19' 10.70      107° 26' 5.97      102° 40'	5.60      4.70 4.00      3.70	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (H4,a) $P1$	S.B. 3-102 M.A. 6-181
Chalcopyrite	$2[\text{CuFeS}_2]$ Tetragonal ( $\bar{4}2m$ )	5.24      10.30	3.03      1.86 1.59      1.21	Chalcopyrite (E11)	S.B. 2-48 M.A. 6-171
Chalybite	$2[\text{FeCO}_3]$ Rhombohedral ( $\bar{3}m$ )	5.76      47° 54'	2.77      2.11 1.95      1.72	Calcite (G1) $R\bar{3}c$	S.B. 1-292 M.A. 6-192
Chessylite	$2[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$ Monoclinic (2/ $m$ )	4.96      10.27 5.83      87° 36'	5.14      3.53 3.49      2.24	Azurite (G74) $P2_1/c$	S.B. 2-81 M.A. 5-180
Chloanthite	$8[(\text{Co}, \text{Ni})\text{As}_2]$ Cubic ( $m\bar{3}$ )	8.25	2.64      2.22 1.87      1.63	Skutterudite (D2) $Im\bar{3}$	S.B. 1-232 M.A. 3-525
Chlorite	$4[\text{Al}_2\text{Mg}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$ Monoclinic (2/ $m$ )	5.30      28.31 9.19      ~83°	13.9      7.01 4.69      3.53	Chlorite (S55) $C2/c$	M.A. 6-45 S.B. 3-156
Chondrodite	$2[\text{Mg}(\text{F}, \text{OH})_2 \cdot 2\text{MgSiO}_4]$ Monoclinic (2/ $m$ )	10.27      14.0 4.73      70° 58'		Chondrodite (S07) $P2_1/b$	S.B. 2-119 M.A. 3-342

Chromite	$8[\text{FeCr}_2\text{O}_4]$ Cubic ( $m\bar{3}m$ )	8-34	2-48 1-58	2-05 1-40	Spinel ( $Il11$ ) $F\bar{4}3m$	S.B. 1-350 M.A. 5-178
Chrysoberyl	$4[\text{BeAl}_2\text{O}_4]$ Orthorhombic ( $mmm$ )	4-24 9-39	3-24 2-08	2-33 1-01	Olvine ( $Il12$ ) $P6mm$	S.B. 1-352 M.A. 3-185
Chrysotile	$4[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$ Monoclinic ( $2/m$ )	14-00 9-24	7-12 3-59	4-57 2-42	Chrysotile ( $S45$ ) $C2/m$	S.B. 2-130 M.A. 4-406
Cinnabar	$3[\text{HgS}]$ Hexagonal ( $32$ )	4-14	3-34 1-07	2-85 1-77	Cinnabar ( $D0$ ) $C3_12$	S.B. 1-87 M.A. 4-26
Clausthalite	$4[\text{PbSe}]$ Cubic ( $m\bar{3}m$ )	6-14	3-06 1-77	2-17 1-37	Rocksalt ( $D1$ ) $Fm\bar{3}m$	S.B. 1-72 M.A. 3-19
Clinohumite	$2[\text{Mg}(\text{F}, \text{OH})_2 \cdot 4\text{Mg}_2\text{SiO}_4]$ Monoclinic ( $2/m$ )	10-24 4-75			Chondrodite ( $S07$ ) $P2_1/b$	S.B. 2-119 M.A. 3-342
Cobaltite	$4[\text{CoAsS}]$ Cubic ( $23$ )	5-55	2-81 2-27	2-49 2-00	Cobaltite ( $F1$ ) $P2_13$	S.B. 1-269 M.A. 8-7
Columbite	$4[(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6]$ Orthorhombic ( $mmm$ )	14-24 5-73	3-61 1-70	2-91 1-43	Columbite ( $E51$ ) $P6cn$	S.B. 2-55 M.A. 4-366
Colusite	$8[\text{Cu}_3(\text{As}, \text{Sb}, \text{V}, \text{Te}, \text{Fe})\text{S}_4]$ Cubic ( $\bar{4}3m$ )	10-60	3-07 1-60	1-88 1-09	Tetrahedrite type $I\bar{4}3m$	S.B. 1-335 M.A. 7-466
Cooperite	$4[\text{PtS}]$ Tetragonal ( $4/mmm$ )	4-01	3-03 1-77	1-93 1-51	Cooperite ( $H17$ ) $P4_1/mmc$	Min. Mag. 23-188 S.B. 2-9
Copper	$4\text{Cu}$ Cubic ( $m\bar{3}m$ )	3-01	2-03 1-23	1-81 1-09	Copper ( $A11$ )	S.B. 1-13
Cordierite	$4[\text{Al}_3\text{Mg}_2\text{Si}_2\text{AlO}_{13}]$ Orthorhombic ( $mmm$ )	17-10 9-78	3-39 3-10	3-31 2-97	Related to Beryl $Cmcn$	M.A. 4-109
Corundum	$2[\text{Al}_2\text{O}_3]$ Rhombohedral ( $\bar{3}m$ )	5-12	2-55 1-74	2-03 1-59	Corundum ( $D51$ ) $R\bar{3}c$	S.B. 1-257 M.A. 2-510
Covellite	$6[\text{CuS}]$ Hexagonal ( $6/mmm$ )	3-80	3-02 2-72	2-82 1-90	Covellite ( $H15$ ) $C6/mmc$	S.B. 2-10 M.A. 5-175
Cristobalite	$4[\text{SiO}_2]$ Tetragonal ( $42$ )	4-96	1-01 2-85	3-13 2-15	Low-cristobalite ( $C30$ ) $P4_12_1$	S.B. 3-25 M.A. 6-329
Crocoite	$4[\text{PbCrO}_4]$ Monoclinic ( $2/m$ )	6-52 7-15	1-34 3-25	3-48 3-01	Not determined $P2_1/n$	M.A. 4-462

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Cryolite	$2[\text{Na}_3\text{AlF}_6]$ Monoclinic (2/m)	5.46 7.80 5.61 89° 49'	2.75 1.94 1.57	Náray-Szabo (1938) $P2_1/n$	M.A. 7-232
Cuprite	$2[\text{Cu}_2\text{O}]$ Cubic ( $m\bar{3}m$ )	4.28	2.46 1.51 2.13 1.29	Cuprite (C3) $Pn\bar{3}m$	S.B. 1-153 M.A. 2-508
Danburite	$4[\text{CaB}_2\text{Si}_2\text{O}_8]$ Orthorhombic ( $mmm$ )	8.75 8.01 7.72	3.59 2.73 2.99 2.66	Danburite (S63) $Pmm$	S.B. 2-153 M.A. 4-462
Descloizite	$4[\text{PbZn}(\text{OH})(\text{VO}_4)]$ Orthorhombic ( $mmm$ )	6.05 9.39 7.56	3.52 2.85 1.65 3.20	Not determined $Pma$	Min. Mag. 23-376
Diamond	2C Cubic ( $m\bar{3}m$ )	3.56	2.06 1.07 0.82 1.26	Diamond (A4) $Fd\bar{3}m$	S.B. 1-19 M.A. 7-80
Diaspore	$4[\text{AlOOH}]$ Orthorhombic ( $mmm$ )	4.40 9.38 2.83	3.98 2.14 2.07	Diaspore (E02) $Pma$	S.B. 2-46 M.A. 6-175
Diopside	$4[\text{CaMg}(\text{SiO}_3)_2]$ Monoclinic (2/m)	9.71 8.89 74° 10'	2.96 1.61 1.41 2.48	Diopside (S41) $C2/c$	S.B. 2-130 M.A. 5-186
Dioptase	$6[\text{H}_2\text{CuSiO}_4]$ Rhombohedral ( $\bar{3}$ )	8.77 114° 42'	7.50 4.16 5.00 2.62	Not determined $R\bar{3}$	M.A. 3-344 M.A. 4-108
Dolomite	$\text{CaMg}(\text{CO}_3)_2$ Rhombohedral ( $\bar{3}$ )	6.00 47° 3'	2.89 2.02 1.80 2.19	Dolomite (G11) $R\bar{3}$	S.B. 1-303 M.A. 3-22
Edingtonite	$2[\text{BaAl}_2\text{Si}_5\text{O}_{10}\cdot 4\text{H}_2\text{O}]$ Tetragonal ( $4_2m$ )	9.59 6.53		Nauroilite (S610) $P4_2/m$	S.B. 3-173 M.A. 5-354
Enargite	$2[\text{Cu}_3\text{AsS}_4]$ Orthorhombic ( $mm$ )	6.46 7.43 6.18	3.21 1.86 2.85 1.59	Enargite (H25) $Pmm$	
Enstatite	$16[\text{MgSiO}_3]$ Orthorhombic ( $mmm$ )	18.20 8.86 5.20	3.15 2.52 1.48 2.90	Enstatite (S45) $Pcca$	S.B. 2-134 M.A. 4-366
Epitidymite	$8[\text{HNaBeSi}_3\text{O}_9]$ Orthorhombic ( $mmm$ )	12.63 7.32 13.58		Epitidymite (S47) $Pma$	S.B. 3-153 M.A. 6-45
Epидote	$2[\text{Ca}_2\text{Al}_2(\text{Al}, \text{Fe})(\text{SiO}_4)_3\text{OH}]$ Monoclinic (2/m)	8.84 5.60 10.10 64° 37'	2.90 1.88 2.40 1.64	Not determined Probably $P2_1/m$	M.A. 5-29
Epsomite	$4[\text{MgSO}_4\cdot 7\text{H}_2\text{O}]$ Orthorhombic (222)	11.94 12.03 6.86	5.90 2.87 4.22 2.66	Not determined $P2_12_12_1$	S.B. 2-429 M.A. 3-345

Euclase	$4[\text{HBeAlSiO}_5]$ Monoclinic (2/m)	4.02 14.24	4.75 70° 44'	Euclase (SO <sub>3</sub> ) $P2_1/c$	S.B. 3-148 M.A. 5-474
Eulytite	$4[\text{Be}_2\text{Si}_3\text{O}_{12}]$ Cubic (43m)	10.27		Eulytite (S1s) $I43d$	S.B. 2-122 M.A. 5-28
Fayalite	$4[\text{Fe}_2\text{SiO}_4]$ Orthorhombic (mmm)	4.80 10.59	0.10	Olivine (H12) $Pnma$	S.B. 1-352
Ferberite	$2[\text{FeWO}_4]$ Monoclinic (2/m)	4.71 5.09	4.95 90°	$\text{MgWO}_4$ (H10) $P2_1/c$	S.B. 2-451
Fluor	$4[\text{CaF}_2]$ Cubic (m3m)	5.47		Fluorite (C1) $Fm3m$	S.B. 1-148 M.A. 7-83
Forsterite	$4[(\text{Mg}, \text{Fe})_2\text{SiO}_4]$ Orthorhombic (mmm)	4.77 10.20	5.00	Olivine (H12) $Pnma$	S.B. 1-352
Franklinite	$8[\text{ZnFe}_2\text{O}_4]$ Cubic (m3m)	8.43		Spinel (H11) $Fd3m$	S.B. 1-350
Gadolinite	$2[\text{Y}_2\text{FeBe}_2\text{Si}_2\text{O}_{10}]$ Monoclinic (2/m)	4.05 7.53	9.87 80.1°	Not determined $P2_1/c$	M.A. 8-92
Gahnite	$8[\text{ZnAl}_2\text{O}_4]$ Cubic (m3m)	8.00		Spinel (H11) $Fd3m$	S.B. 1-350
Galena	$4[\text{PbS}]$ Cubic (m3m)	5.92		Rocksalt (H1) $Fm3m$	S.B. 1-72 M.A. 6-109
Gehlenite	$2[\text{Ca}_2\text{Al}_2\text{SiO}_7]$ Tetragonal (42m)	7.69	5.10	Hardystonite (S53) $P4_2/m$	S.B. 2-140 M.A. 5-28
Gersdorffite	$4[(\text{Ni}, \text{Co}, \text{Fe})\text{AsS}]$ Cubic (23)	5.05		Cobaltite (F1)	S.B. 1-269 M.A. 8-7
Gibbsite	$8[\text{Al}(\text{OH})_3]$ Monoclinic (2/m)	8.62 5.06	9.70 85° 26'	Hydrargillite (D7) $P2_1/c$	S.B. 2-38 M.A. 5-471
Gismondine	$8[\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}]$ Orthorhombic (mmm)	13.03 14.30	10.60	Not determined $Cmmm$	M.A. 7-398
Goethite	$4[\text{FeOOH}]$ Orthorhombic (mmm)	4.04 10.0	3.03	Diaspore (E2) $Pnma$	S.B. 2-46 M.A. 5-179
Gold	4Au Cubic (m3m)	4.07		Copper (A1) $Fm3m$	S.B. 1-13 S.B. 2-103

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Graphite	4C Hexagonal ( <i>6/mmm</i> )	2.46 6.80	3.40 1.68 2.06 1.23	Graphite ( <i>A9</i> ) <i>C6/mmc</i>	S.B. 1-28 M.A. 3-335
Greenockite	2[CdS] Hexagonal ( <i>Cmm</i> )	4.14 6.72	3.55 2.06 1.89	Wurite ( <i>B4</i> ) <i>C6mc</i>	S.B. 1-78 M.A. 3-20
Grossular	8[Ca <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> ] Cubic ( <i>m3m</i> )	11.84	2.97 1.64	Garnet ( <i>S14</i> ) <i>Ia3d</i>	S.B. 1-363 M.A. 4-111
Grunerite	2[H <sub>2</sub> Fe <sub>7</sub> (SiO <sub>3</sub> ) <sub>8</sub> ] Monoclinic ( <i>2/m</i> )	9.4 17.9 5.27 ~74°	2.66 1.58	Tremolite ( <i>S42</i> ) <i>C2/m</i>	S.B. 2-131 M.A. 4-278
Gudmundite	4[FeSbS] Monoclinic ( <i>2/m</i> )	6.02 5.93 6.02 67° 52'		Arsenopyrite ( <i>E7</i> ) <i>P2<sub>1</sub>/c</i>	S.B. 4-30 M.A. 7-387
Gypsum	4[CaSO <sub>4</sub> ·2H <sub>2</sub> O] Monoclinic ( <i>2/m</i> )	5.67 15.15 6.51 61° 37'	7.20 3.02 2.07	Gypsum ( <i>H46</i> ) <i>I2/a</i>	S.B. 4-47 M.A. 6-413
Haematite	2[Fe <sub>2</sub> O <sub>3</sub> ] Rhombohedral ( <i>3m</i> )	5.41 55° 14'	2.69 1.84 1.68	Corundum ( <i>D51</i> ) <i>R3c</i>	S.B. 1-240 M.A. 6-43
Halloysite	2[H <sub>4</sub> Si <sub>2</sub> Al <sub>2</sub> O <sub>9</sub> ] Monoclinic ( <i>m</i> )	5.20 8.92 10.25 80°	10.1 3.40 2.56	Partially determined <i>Cm</i>	M.A. 7-422
Hambergite	8[Be <sub>2</sub> BO <sub>3</sub> (OH)] Orthorhombic ( <i>mmm</i> )	9.73 12.18 4.42		Hambergite ( <i>G72</i> ) <i>Pbca</i>	S.B. 2-78 M.A. 5-27
Hardystonite	2[Ca <sub>2</sub> ZnSi <sub>2</sub> O <sub>7</sub> ] Tetragonal ( <i>42m</i> )	7.83 4.99		Hardystonite ( <i>S53</i> ) <i>P4<sub>2</sub>/m</i>	S.B. 2-146 M.A. 4-462
Harmotome	2[BaAl <sub>2</sub> Si <sub>6</sub> O <sub>16</sub> ·6H <sub>2</sub> O] Monoclinic ( <i>2/m</i> )	9.80 14.10 8.60 55° 10'	8.11 6.25 4.07	Not determined <i>P2<sub>1</sub>/m</i>	M.A. 7-346
Hauerite	4[MnS <sub>2</sub> ] Cubic <i>m3</i>	6.10	3.04 2.49 2.15	Pyrite ( <i>C2</i> ) <i>Pa3</i>	S.B. 1-150 M.A. 6-38
Hausmannite	8[Mn <sub>3</sub> O <sub>4</sub> ] Tetragonal ( <i>4/mmm</i> )	8.14 9.42	2.76 2.36 1.57	Deformed Spinel ( <i>H11</i> ) <i>I4/amd</i>	S.B. 1-350 M.A. 3-342
Häuytite	Na <sub>2</sub> (Ca, K) <sub>2</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(SO <sub>4</sub> ) <sub>2</sub> Cubic ( <i>3m</i> )	9.10		Häuytite ( <i>S69</i> ) <i>P43n</i>	S.B. 3-166
Helvite	2[(Mn, Fe) <sub>4</sub> (BeSiO <sub>3</sub> ) <sub>3</sub> S] Cubic ( <i>3m</i> )	8.25		Sodalite ( <i>S62</i> ) <i>P43n</i>	S.B. 2-150 M.A. 4-367

Hemimorphite	$4[\text{H}_2\text{Zn}_2\text{SiO}_5]$ Orthorhombic ( <i>mm</i> )	8-38 10-70	5-11	6-51 9-27	5-35 3-08	Hemimorphite ( <i>S22</i> ) <i>Imm</i>	S.B. 2-125 M.A. 5-187
Hornblende	$2[\text{H}_2(\text{Ca}, \text{Na}, \text{K})_2-3(\text{Mg}, \text{Fe}, \text{Al})_3(\text{Si}, \text{Al})\text{O}_{13}]$ Monoclinic ( <i>2/m</i> )	9-8 17-9	5-28 ~71°	8-00 2-71	3-13 2-17	Tremolite ( <i>S42</i> ) <i>C2/m</i>	S.B. 2-131 M.A. 4-278
Hübnerite	$2[\text{MnWO}_4]$ Monoclinic ( <i>2/m</i> )	4-82 5-76	4-07 80° 7'	4-83 2-97	3-77 2-49	$\text{MgWO}_4$ ( <i>I70</i> ) <i>P2/c</i>	S.B. 2-85 S.B. 2-451
Humite	$4[\text{Mg}(\text{F}, \text{OH})_2\text{Mg}_2\text{SiO}_4]$ Orthorhombic ( <i>mmm</i> )	4-74 10-23	20-80			Chondrodite series ( <i>S7</i> ) <i>P6mm</i>	S.B. 2-119 M.A. 3-342
Hydroxyapatite	$2[\text{Ca}_3(\text{OH})(\text{PO}_4)_3]$ Hexagonal ( <i>6/m</i> )	9-42	0-04	3-44 2-27	2-70 1-04	Apatite (F-type) ( <i>I167</i> ) <i>C63/m</i>	S.B. 2-00 M.A. 7-106
Ice	$4[\text{H}_2\text{O}]$ Hexagonal ( <i>6/mmm</i> )	4-54	7-41			$\beta$ -Tridymite ( <i>C19</i> ) <i>C6/mmc</i>	S.B. 1-171 M.A. 4-273
Idocrase	$4[\text{Ca}_{10}\text{Al}_4(\text{Mg}, \text{Fe})_2\text{Si}_6\text{O}_{34}(\text{OH})_4]$ Tetragonal ( <i>4/mmm</i> )	15-63	11-83	2-74 2-45	2-50 1-63	Vesuvianite ( <i>S23</i> ) <i>P4/mnc</i>	S.B. 2-126 M.A. 5-28
Ilmenite	$2[\text{FeTiO}_3]$ Rhombohedral ( $\bar{3}$ )	5-52	54° 40'	2-72 2-23	2-53 2-03	Ilmenite ( <i>E22</i> ) <i>R3</i>	S.B. 2-60 M.A. 6-13
Iridosmine	$2(\text{Ir}, \text{Os})$ Hexagonal ( <i>6/mmm</i> )	2-90	4-60			Magnesium ( <i>A3</i> ) <i>C6/mmc</i>	S.B. 1-525
Iron	$2\text{Fe}$ Cubic ( <i>m3m</i> )	2-80		2-01 1-67	1-43 1-01	Tungsten ( <i>A2</i> ) <i>Im3m</i>	S.B. 1-15
Jacobsite	$4[\text{MgMn}(\text{Fe}_2\text{O}_4)_2]$ Cubic ( <i>m3m</i> )	8-42				Spinel ( <i>I11</i> ) <i>Fd3m</i>	S.B. 1-350 M.A. 4-13
Jamesonite	$4(\text{Pb}_4\text{FeSb}_6\text{S}_{14})$ Monoclinic	15-64 19-01	4-03 88° 12'	3-10 2-72	2-51 2-28	Not determined	M.A. 8-7
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ Rhombohedral ( <i>3m</i> )	7-03	61° 37'	3-08 1-96	2-27 1-51	Hendricks ( <i>I937</i> ) <i>R3m</i>	M.A. 7-57
Jordanite	$\text{Pb}_{27}\text{As}_{14}\text{S}_{44}$ Monoclinic <i>2/m</i>	8-89 31-65	8-40 61° 39'	3-10 2-10	2-22 1-82	Not determined <i>P21/m</i>	M.A. 8-7
Kaliohillite	$54[\text{KAlSiO}_4]$ Hexagonal ( <i>62</i> )	27-0	8-50	3-10 2-59	3-09 1-65	Not determined <i>C632</i>	M.M. 22-569
Kalsilite	$2[\text{KAlSiO}_4]$ Hexagonal ( <i>62</i> )	5-17	8-67	4-35 3-11	3-97 2-59	Not determined <i>C632</i>	M.M. 26-218

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Kamafite	$2[\text{Fe,Ni}]$ Cubic ( $m\bar{3}m$ )	2.87	2.03 1.17	Tungsten ( $A2$ ) $Im\bar{3}m$	S.B. 1-15, 523 M.A. 3-259
Kaolinite	$4[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ Monoclinic ( $m$ )	5.14 8.90 79° 48'	7.20 3.59 2.34	Gruner (1932) $Cc$	M.A. 5-187
Krennerite	$8[\text{AuTe}_2]$ Orthorhombic ( $mmm$ )	16.51 8.80 4.45	3.05 2.24 2.12	Krennerite ( $C46$ ) $Pma$	S.B. 4-15 M.A. 7-81
Kyanite	$4[\text{Al}_2\text{SiO}_5]$ Anorthic ( $\bar{1}$ )	7.09 7.72 5.56 90° 51' 101° 2' 105° 44'	3.33 2.52 2.37	Kyanite ( $H51$ ) $P\bar{1}$	S.B. 1-427 M.A. 4-159
Labradorite	$4[(\text{Ca},\text{Na})(\text{Si},\text{Al})_2\text{O}_6]$ Anorthic ( $\bar{1}$ )	8.21 12.95 14.16 93° 31' 116° 3' 89° 55'	3.22 2.53 2.53	Near Albite ( $S68$ ) $P\bar{1}$	S.B. 3-164 M.A. 6-177
Laurite	$4[\text{RuS}_2]$ Cubic ( $m\bar{3}$ )	5.59		Pyrite ( $C2$ ) $Pn\bar{3}$	S.B. 1-150 M.M. 23-188
Lead	$4\text{Pb}$ Cubic ( $m\bar{3}m$ )	4.01	2.84 1.74	Copper ( $A1$ ) $Fm\bar{3}m$	S.B. 1-13 M.A. 3-340
Lepidocrocite	$4[\text{FeOOH}]$ Orthorhombic ( $mmm$ )	3.87 12.4	6.20 2.45	Lepidocrocite ( $E4$ ) $Cmcn$	S.B. 3-67 M.A. 5-179
Lepidolite	$2[\text{K}(\text{Li},\text{Al})_2(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH},\text{F})_2]$ Monoclinic ( $m$ )	5.3 9.2	10.0 2.56	Hendricks (1939) $Cm$	M.A. 7-496
Leucite	$16[\text{KAlSi}_2\text{O}_6]$ Tetragonal ( $42$ )	12.95	3.41 2.92	Not determined $I4_12$	M.A. 6-412
Libethenite	$4[\text{Cu}_2(\text{OH})\text{PO}_4]$ Orthorhombic ( $mmm$ )	8.43 8.08	5.80 2.91	Not determined $Pnmn$	M.A. 7-495
Linnaeite	$8[\text{Co}_3\text{S}_4]$ Cubic ( $m\bar{3}m$ )	9.40	2.82 1.82	Spinel ( $H11$ ) $Fd\bar{3}m$	S.B. 1-350 M.A. 3-339
Litharge	$2\text{PbO}$ Tetragonal ( $4/mmm$ )	3.95	3.06 2.72	Phosphonium Iodide ( $H10$ ) $P4/mnm$	S.B. 1-89 M.A. 8-216
Löllingite	$2[\text{FeAs}_2]$ Orthorhombic ( $mmm$ )	2.85 5.25	3.45 2.43	Marcasite ( $C18$ ) $Pnmn$	S.B. 1-495 M.A. 5-175



Mineral	Chemical Formula	Crystal System	Angle	2θ	hkl	Ref.
Magnesite	$2\text{MgCO}_3$	Rhombohedral ( $\bar{3}m$ )	48°	2.70 2.10	Calcite (G1) $R\bar{3}c$	S.B. 1-202 M.A. 6-102
Magnetite	$8[\text{Fe}_3\text{O}_4]$	Cubic ( $m\bar{3}m$ )		2.06 2.09	Spinel ( $I\bar{4}11$ ) $Fd\bar{3}m$	S.B. 1-350 M.A. 4-334
Malachite	$4[\text{CuCO}_3, \text{Cu}(\text{OH})_2]$	Monoclinic ( $2/m$ )	3-18 88° 57'	5.77 2.82	Not determined $P2_1/c$	M.A. 5-180
Manganite	$8[\text{MnO}(\text{OH})]$	Monoclinic ( $2/m$ )	5.70 90°	3.80 1.06	Manganite (E0) $P2_1/c$	S.B. 4-28 M.A. 6-411
Manganosite	$4[\text{MnO}]$	Cubic ( $m\bar{3}m$ )		2.56 1.57	Rocksalt ( $H1$ ) $Fm\bar{3}m$	S.B. 1-72 M.A. 3-179
Marcasite	$2[\text{FeS}_2]$	Orthorhombic ( $mmm$ )	5.39	2.09 2.31	Marcasite (C18) $Pnnm$	S.B. 1-405 M.A. 5-22
Margarite	$4[\text{CaAl}_2(\text{Al}_2\text{Si}_2\text{O}_{10})(\text{OH})_2]$	Monoclinic $2/m$	19-44 70° 12'		Not determined	M.A. 4-32
Matlockite	$2[\text{PbFCl}]$	Tetragonal ( $4/mmm$ )	7.21	3.54 2.25	PbFCl (E1)	S.B. 2-45 M.A. 5-475
Melanterite	$8[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$	Monoclinic ( $2/m$ )	20.03 73° 44'	4.90 3.23	Not determined $P2_1/c$	M.A. 8-10
Mellite	$2[(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_7]$	Tetragonal ( $\bar{4}2m$ )	5.01	3.14 1.75	Hardystonite (S53) $P4_2/m$	S.D. 2-146 M.A. 4-367
Mesolite	$8[\text{Ca}_2\text{Na}_2\text{Al}_6\text{Si}_9\text{O}_{36} \cdot 8\text{H}_2\text{O}]$	Monoclinic (2)	13-14 90°		Not determined $C_2$	S.B. 3-103 M.M. 23-421
Metacinnabarite	$4\text{HgS}$	Cubic ( $\bar{4}3m$ )		3.36 2.07	Blende (H3) $F\bar{4}3m$	S.B. 1-76 M.A. 2-510
Miargyrite	$8[\text{AgSbS}_2]$	Monoclinic ( $2/m$ )	12.83 81° 22'	3.42 2.71	Not determined $C2/c$	M.A. 7-397
Millerite	$3[\text{NiS}]$	Rhombohedral ( $\bar{3}m$ )	110° 35'	2.75 1.31	Millerite (H13) $R\bar{3}m$	S.B. 2-6 M.A. 5-175
Mimetite	$2[\text{Pb}_2\text{Cl}(\text{AsO}_4)_3]$	Hexagonal ( $6/m$ )	7.43	3.05 2.10	Apatite (H57)(Cl) $C6_3/m$	S.B. 2-99
Minlum	$4[\text{Pb}_3\text{O}_4]$	Tetragonal ( $\bar{4}2m$ )	6.66	3.35 2.76	Not determined $P4_2$	M.A. 8-216

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Mispickel	8[FeAsS] Monoclinic (2/m)	9.51 5.65 6.42 90°	2.63 1.80 1.62	Arsenopyrite (P77) $P2_1/c$	S.B. 4-30 M.A. 6-409
Molybdenite	2[MoS <sub>2</sub> ] Hexagonal (6/mmm)	3.15 12.30	6.16 2.26 1.83	Molybdenite (C7) $C6/mmc$	S.B. 1-164 M.A. 2-196
Monazite	4[(La,Ce,Y)PO <sub>4</sub> ] Monoclinic (2/m)	6.76 7.00 6.42 76° 50'		Not determined $P2_1/n$	M.A. 7-494
Monticellite	4[(Ca,Mg) <sub>2</sub> SiO <sub>4</sub> ] Orthorhombic (mmm)	4.82 11.08 6.37	3.56 1.79 1.58	Olivine (H12) $Pnma$	S.B. 1-352 M.A. 3-342
Montmorillonite	2[Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·mH <sub>2</sub> O] Orthorhombic	5.09 8.83 15.2	12.2 3.14 2.56	Not determined (A three layer structure)	M.A. 7-422
Mordenite	4[(Ca,Naz,Kz)Al <sub>2</sub> Si <sub>10</sub> O <sub>23</sub> ·7H <sub>2</sub> O] Orthorhombic (mmm)	18.25 20.35 7.50		Not determined $Cmcm$	M.M. 25-212
Mullite	3[Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub> ] Orthorhombic	14.98 15.26 5.74	5.41 2.70 3.39 2.54	Near to Sillimanite (S3)	S.B. 2-112 M.A. 4-32
Muscovite	4[K(OH,F) <sub>2</sub> Al <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )] Monoclinic (2/m)	5.18 9.02 20.04 84° 30'	9.96 2.56 1.99	Muscovite (S51) $C2/c$	S.B. 2-143 M.A. 4-467
Natrolite	8[Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> ·2H <sub>2</sub> O] Orthorhombic (mm)	18.31 18.66 6.60	6.42 3.10 2.82	Natrolite (S610) $Fdd$	S.B. 3-168 M.M. 23-343
Nepheline	8[NaAlSiO <sub>4</sub> ] Hexagonal (6)	9.97 8.35	4.21 3.23 3.81 3.00	Not determined $C6_3$	M.M. 22-569
Niecolite	2[NiAs] Hexagonal (6/mmm)	3.61 5.03	2.62 1.80 1.33	Niecolite (B8) $C6/mmc$	S.B. 1-84 M.A. 3-19
Nitratine	4[KNO <sub>3</sub> ] Orthorhombic (mmm)	5.40 9.14 6.41	3.03 1.80 1.65	Aragonite (C2) $Pnma$	S.B. 1-295
Nitre	2[NaNO <sub>3</sub> ] Rhombohedral ( $\bar{3}m$ )	6.32 47° 14'	3.77 2.66 3.03 2.19	Calcite (G1) $R\bar{3}c$	S.B. 1-204
Norbergite	4[Mg(F,OH) <sub>2</sub> Mg <sub>2</sub> SiO <sub>4</sub> ] Orthorhombic (mmm)	4.70 10.2 8.72	3.08 2.26 1.74	Chondrodite series (S7) $Pnma$	S.B. 2-119 M.A. 4-159
Northupite	16[Na <sub>3</sub> MgCl(CO <sub>3</sub> ) <sub>2</sub> ] Cubic ( $m\bar{3}m$ )	14.05		Northupite (G73) $Fd\bar{3}m$	S.B. 2-80 M.A. 5-451

Mineral	Chemical Formula	Crystal System	d <sub>hkl</sub>	2θ	hkl	Crystal System	Mineral	Chemical Formula	Crystal System	d <sub>hkl</sub>	2θ	hkl
Noson	$\text{Na}_3(\text{AlSiO}_4)_6\text{SO}_4$	Cubic (43m)	0.03				Sodalite (S02)		$P4_3m$			
Olivine	$4[\text{Cu}_2(\text{OH})\text{AsO}_4]$	Orthorhombic (222)	8.16	5.86			Not determined		$P2_12_12_1$			
Olivine	$4[\text{Mg}_2\text{SiO}_4]$	Orthorhombic (mmm)	4.76	5.00			Olivine (H12)		$Pmma$			
Orthoclase	$4[\text{KAlSi}_3\text{O}_8]$	Monoclinic (2/m)	10.21				Smilite (S07)		$C2/m$			
Osbornite	$4[\text{TiN}]$	Cubic (m3m)	8.4	7.1			Reckasalt (B1)		$Fm3m$			
Osmiridium	$4[\text{Ir}_2\text{O}_3]$	Cubic (m3m)	12.9	61°			Copper (A1)		$Fm3m$			
Paragonite	$4[(\text{Na}, \text{K})(\text{OH}, \text{F})_2\text{Al}_2(\text{AlSi}_3\text{O}_{10})]$	Monoclinic (2/m)	3.84				Muscovite (S51)		$C2/c$			
Pectolite	$2[\text{HfNaCa}_2(\text{SiO}_3)_3]$	Anorthic	5.12	18.05			Not determined					
Pentlandite	$4[(\text{Ni}, \text{Fe})_9\text{S}_3]$	Cubic (m3m)	9.97				$\text{Co}_3\text{S}_4$ (D30)		$Fm3m$			
Periclase	$4[\text{MgO}]$	Cubic (m3m)	7.91	30°			Reckasalt (H1)		$Fm3m$			
Perovskite	$8[\text{CaTiO}_3]$	Cubic (m3m)	7.03	03° 10'			Perovskite (F21)		$Pm3m$			
Petalite	$4[\text{LiAl}(\text{Si}_3\text{O}_8)_2]$	Monoclinic	7.05	103° 0'			Not determined					
Pharmacosiderite	$\text{Al}_5\text{As}_5\text{O}_{12}(\text{OH})_6 \cdot 6\text{H}_2\text{O}$	Cubic (43m)	10.02	15.17			Haasite (1937)		$P4_3m$			
Phenakite	$6[\text{Be}_2\text{SiO}_4]$	Rhombohedral (3)	1.20	67° 10'			Phenakite (H13)		$R3$			
Phillipsite	$2[\text{KCaAl}_3\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}]$	Monoclinic (2)	1.20	103° 1'			Not determined		$P2_1$			
Phosgenite	$2[\text{PbCl}_2 \cdot \text{PbCO}_3]$	Tetragonal (42)	8.12	4.1			Phosgenite (G75)		$P4_21$			

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.		V. Structure-type and space-group.	VI. References.
Platinum	4Pt Cubic ( <i>m3m</i> )	3.01	2.25 1.38	1.05 1.18	Copper ( <i>A1</i> ) <i>Fm3m</i>	S.B. 1-13 M.M. 23-188
Pollucite	$16[\text{CsAlSi}_2\text{O}_6 \cdot x\text{H}_2\text{O}]$ Pseudocubic ( <i>4/mmm</i> )	13.74	3.67 2.03	3.43 2.42	Analcime ( <i>S01</i> ) <i>I4/acd</i>	S.B. 2-148 M.A. 7-238
Polydymite	$8[\text{Ni}_3\text{S}_4]$ Cubic ( <i>m3m</i> )	0.41			Spinell ( <i>H11</i> ) <i>Fd3m</i>	S.B. 1-350 M.A. 3-330
Portlandite	$\text{Ca}(\text{OH})_2$ Hexagonal ( $\bar{3}m$ )	3.04	4.03 1.03	2.03 1.70	Cadmium Iodide ( <i>C0</i> ) <i>C3m</i>	S.B. 1-101 M.M. 23-410
Prehnite	$2[\text{H}_2\text{Ca}_2\text{Al}_2(\text{SiO}_3)_3]$ Orthorhombic ( <i>mm</i> )	4.05 5.52	3.40 3.05	3.23 2.54	Not determined <i>Pma</i>	M.A. 5-186
Proustite	$2[\text{Ag}_3\text{AsS}_3]$ Rhombohedral ( <i>3m</i> )	0.84	3.20 2.53	2.75 1.04	Harker (1030) <i>R3c</i>	M.A. 6-400
Pseudobrookite	$4[\text{Fe}_2\text{TiO}_5]$ Orthorhombic ( <i>mmm</i> )	0.70 0.03			Pseudobrookite ( <i>E41</i> ) <i>Cmcm</i>	S.B. 2-53 M.A. 4-274
Pselomelane	$2[\text{H}_2\text{RMn}_4\text{O}_{10}]$ Orthorhombic	0.1 13.7	3.35 2.43	2.70 1.63	Not determined "	M.M. 24-521
Pyrrargyrite	$2[\text{Ag}_3\text{SbS}_3]$ Rhombohedral ( <i>3m</i> )	7.0	3.35 2.79	3.20 2.55	Harker (1030) <i>R3c</i>	M.A. 6-400
Pyrite	$4[\text{FeS}_2]$ Cubic ( <i>m3</i> )	5.41	2.70 1.01	2.42 1.63	Pyrite ( <i>C2</i> ) <i>Pa3</i>	S.B. 1-150 M.A. 5-310
Pyrochlore	$8[(\text{Na,Ca})_2(\text{Nb,Ti})_2(\text{O,F})_7]$ Cubic ( <i>m3m</i> )	10.38			Koppleite ( <i>E81</i> ) <i>Fd3m</i>	S.B. 2-58 M.A. 5-185
Pyrochroite	$[\text{Mn}(\text{OH})_2]$ Hexagonal ( $\bar{3}m$ )	3.34	4.62 2.38	2.43 1.84	Cadmium Iodide ( <i>C0</i> ) <i>C3m</i>	S.B. 1-101 M.A.
Pyroalusite	$2[\text{MnO}_2]$ Tetragonal ( <i>4/mmm</i> )	4.38	3.11 1.62	2.40 1.30	Rutile ( <i>C4</i> ) <i>Pa4/mmm</i>	S.B. 1-155 M.M. 24-521
Pyromorphite	$2[\text{Pb}_3\text{O}(\text{PO}_4)_3]$ Hexagonal ( <i>6/m</i> )	0.05	2.02 1.49	1.52 1.20	Apatite ( <i>H57, F</i> ) <i>C63/m</i>	S.B. 2-09 M.A. 5-184
Pyrope	$8[\text{Mg}_3\text{Al}_2\text{Si}_5\text{O}_{12}]$ Cubic ( <i>m3m</i> )	11.51	2.80 1.60	2.63 1.54	Garnet ( <i>S14</i> ) <i>Ia3d</i>	S.B. 3-150 M.A. 4-111

Pyrophyllite	$4[Al_2Si_4O_{10}(OH)_2]$ Monoclinic (2/m)	5.14 8.90	18.55 80° 5'	8.97 3.04	4.53 2.40	Pyrophyllite (S56) $C2/c$	S.B. 3-160 M.A. 6-45
Pyrrhotine	$2[FeS]$ Hexagonal (6/mmm)	3.45	5.67	2.07 2.06	2.65 1.71	Niccolite (D8) $C6/mmc$	S.B. 1-84 M.A. 8-0
Quartz	$3[SiO_2]$ Hexagonal (32)	4.90	5.39	4.25 1.82	3.35 1.38	Quartz (C8) $C3_1/2$	S.B. 1-100, 3-21 M.A. 3-183
Rammelsbergite	$2[NiAs_2]$ Orthorhombic (mmm)	3.53 4.78	5.78	2.76 1.83	2.49 1.42	Not determined $Pnnm$	M.A. 7-469
Realgar	$16[AsS]$ Monoclinic (2/m)	9.27 13.50	6.56 73° 27'	5.40 2.93	3.15 2.71	Not determined $P2_1/c$	M.A. 6-169
Rhodochrosite	$2[MnCO_3]$ Rhombohedral ( $\bar{3}m$ )	5.84	47° 40'	3.65 2.36	2.81 1.76	Calcite (G1) $R\bar{3}c$	S.B. 1-292
Rhodonite	$2[CaMn_4(SiO_3)_3]$ Anorthic	7.77 12.45 6.74	85° 10' 91° 4' 111° 29'	2.07 2.70	2.90 1.43	Not determined	M.A. 4-103
Romeite	$8[CaNaSb_2O_6(OH)]$ Cubic ( $m\bar{3}m$ )	10.20		2.96 1.55	1.31 1.13	Antimony Tetroxide (D62) $F\bar{4}3m$	S.B. 3-54 M.A. 5-184
Rutile	$2[TiO_2]$ Tetragonal (4/mmm)	4.53	2.95	3.20 2.17	2.16 1.67	Rutile (C4) $P1/mnm$	S.B. 1-155 M.A. 3-429
Safflorite	$4[(Co,Fe)As_2]$ Orthorhombic	6.35 4.86	5.50	2.60 1.87	2.37 1.61	Not determined	M.A. 4-26
Salammoniac	$NH_4Cl$ Cubic ( $m\bar{3}m$ )	3.96		3.85 1.92	2.72 1.57	Calcium Chloride (D2) $Pm\bar{3}m$	S.B. 1-107
Salt	$4[NaCl]$ Cubic ( $m\bar{3}m$ )	5.63		2.81 1.63	1.99 1.26	Rocksalt (H1) $Fm\bar{3}m$	S.B. 1-72 M.A. 3-426
Sassolite	$3[B(OH)_3]$ Anorthic	7.01 7.01 6.56	92° 30' 101° 10' 120°			Not determined	M.A. 6-43
Scapolite	$2[Na_4Cl(AlSi_3O_9)]$ Tetragonal (4/m)	12.09	7.53	3.39 2.63	3.00 1.90	Scapolite (S61) $I1/m$	S.B. 2-155 M.A. 5-186
Scheelite	$4[CaWO_4]$ Tetragonal (4/m)	5.26	11.41	4.76 1.92	3.09 1.53	Scheelite (H4) $I1_1/a$	S.B. 1-317 M.A. 3-316
Scolecite	$8[CaAl_2Si_3O_{10} \cdot 3H_2O]$ Monoclinic (m)	18.18 18.95	6.54 89° 21'			Natrolite type (S610) $Cc$	S.B. 3-171 M.M. 24-227

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Scorodite	$8[\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}]$ Orthorhombic ( <i>mmm</i> )	8.92 10.30	10.01	Not determined <i>Pbca</i>	M.A. 8-140
Senarmontite	$16[\text{Sb}_2\text{O}_3]$ Cubic ( <i>m3m</i> )	11.14	3.22 1.96	Senarmontite ( <i>D61</i> ) <i>Fd3m</i>	S.B. 1-245
Sillimanite	$4[\text{Al}_2\text{SiO}_5]$ Orthorhombic ( <i>mmm</i> )	7.43 7.58	5.74	Sillimanite ( <i>S3</i> ) <i>Pnma</i>	S.B. 2-112 M.A. 4-32
Silver	$4\text{Ag}$ Cubic ( <i>m3m</i> )	4.08	2.36 1.45	Copper ( <i>A1</i> ) <i>Fm3m</i>	S.B. 1-13 M.A. 7-228
Skutterudite	$8[\text{CoAs}_2]$ Cubic ( <i>m3</i> )	8.19	2.64 1.02	Skutterudite ( <i>D2</i> ) <i>Im3</i>	S.B. 1-232 M.A. 3-525
Smaltite	$8[\text{CoAs}_2]$ Cubic ( <i>m3</i> )	8.27	2.62 1.62	Skutterudite ( <i>D2</i> ) <i>Im3</i>	S.B. 1-232 M.A. 3-525
Smithsonite	$2[\text{ZnCO}_3]$ Rhombohedral ( $\bar{3}m$ )	5.67	48° 26'	Calcite ( <i>G1</i> ) <i>R3c</i>	S.B. 1-293 S.B. 2-391
Sodalite	$2[\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}]$ Cubic ( $\bar{4}3m$ )	8.87	3.47 2.31	Sodalite ( <i>S62</i> ) <i>P43n</i>	S.B. 2-150 M.A. 4-367
Sperryite	$4[\text{PtAs}_2]$ Cubic ( <i>m3</i> )	5.93	3.57 2.34	Pyrite ( <i>O2</i> ) <i>Pc3</i>	S.B. 1-150 M.M. 23-188
Spessartine	$8[\text{Mn}_2\text{Al}_2\text{Si}_2\text{O}_{12}]$ Cubic ( <i>m3m</i> )	11.60	1.79 1.14	Garnet ( <i>S14</i> ) <i>Ia3d</i>	S.B. 1-363 S.B. 3-150
Sphene	$4[\text{CaTiSiO}_5]$ Monoclinic ( <i>2/m</i> )	6.55 8.70	2.60 1.55	Titanite ( <i>S6</i> ) <i>C2/c</i>	S.B. 2-117 M.A. 4-281
Spinel	$8[\text{Al}_2\text{MgO}_4]$ Cubic ( <i>m3m</i> )	8.08	3.20 2.59	Spinel ( <i>H11</i> ) <i>Fd3m</i>	S.B. 1-350 M.A. 5-179
Spodumene	$4[\text{LiAl}(\text{SiO}_3)_2]$ Monoclinic ( <i>2/m</i> )	9.50 8.30	2.41 1.42	Dioptside ( <i>S41</i> ) <i>C2/c</i>	S.B. 2-130 M.A. 5-186
Stannite	$2[\text{Cu}_2\text{FeSnS}_4]$ Tetragonal ( $\bar{4}2m$ )	5.46	4.35 2.90	Stannite ( <i>H26</i> ) <i>I42m</i>	S.B. 3-06 M.A. 6-39
Staurolite	$4[\text{Fe}(\text{OH})_2\text{Al}_2\text{Si}_2\text{O}_{10}]$ Orthorhombic ( <i>mmm</i> )	7.82 16.52	3.11 1.63	Staurolite ( <i>S4</i> ) <i>Cmcm</i>	S.B. 2-113 M.A. 4-160

Stephanite	$4[\text{Ag}_3\text{SbS}_4]$ Orthorhombic ( <i>mmm</i> )	7-85 12-48	8-58	3-06 2-75	2-90 2-56	Not determined <i>Cmcm</i>	M.A. 5-176
Stibiconite	$16[\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ Cubic ( <i>m3m</i> )	10-24		2-88 1-54	1-79 1-42	Antimony Tetroxide ( <i>D02</i> ) <i>Fd3m</i>	S.B. 3-54
Stibnite	$4[\text{Sb}_2\text{S}_3]$ Orthorhombic ( <i>mmm</i> )	11-20 11-28	3-83	3-55 1-04	3-05 1-09	Antimonite ( <i>D53</i> ) <i>Pnma</i>	S.B. 3-40 M.A. 5-405
Stilbite	$2[\text{NaCa}_2\text{Al}_3\text{Si}_3\text{O}_{36} \cdot 14\text{H}_2\text{O}]$ Monoclinic ( <i>2/m</i> )	13-00 18-13	11-29 52°	0-22 4-09	4-74 3-04	Not determined <i>C2/m</i>	M.A. 6-525
Strontianite	$4[\text{SrCO}_3]$ Orthorhombic ( <i>mmm</i> )	5-12 8-40	0-08	3-53 2-05	2-45 1-90	Aragonite ( <i>G2</i> ) <i>Pcmm</i>	S.B. 1-295 M.A. 5-180
Sulphohalite	$4[\text{2Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{NaF}]$ Cubic ( <i>m3m</i> )	10-08		1-70 1-27	1-46 0-91	Sulphohalite ( <i>H53</i> ) <i>Fm3m</i>	S.B. 3-118 M.A. 6-182
Sulphur	128 S Orthorhombic ( <i>mmm</i> )	10-48 12-92	24-55	3-85 3-10	3-21 2-85	Sulphur ( <i>A4</i> ) <i>Fdd</i>	S.B. 3-4, 215 M.A. 3-17
Sulvanite	$\text{Cu}_3\text{VS}_4$ Cubic ( $\sqrt{3}m$ )	5-37		5-20 2-40	3-11 1-62	Sulvanite ( <i>H24</i> ) <i>P13m</i>	S.B. 3-04 M.A. 5-310
Swedenborgite	$2[\text{NaBe}_4\text{SbO}_7]$ Hexagonal ( <i>6mm</i> )	5-42	8-80			Swedenborgite ( <i>E92</i> ) <i>C6mc</i>	S.B. 3-09 M.A. 5-321
Sylvanite	$2[\text{AuAgTe}_4]$ Monoclinic ( <i>2/m</i> )	8-94 1-48	14-59 31° 34'	3-95 2-06	3-05 21-2	Tunnell ( <i>1941</i> ) <i>P2/c</i>	M.A. 8-214
Sylvine	$4\text{KCl}$ Cubic ( <i>m3m</i> )	0-23		3-13 1-81	2-21 1-40	Rocksalt ( <i>B1</i> ) <i>Fm3m</i>	S.B. 1-72
Taenite	$4[\text{Ni}_4\text{Fe}]$ Cubic ( <i>m3m</i> )	3-59		2-09 1-28	1-80 1-09	Copper ( <i>A1</i> ) <i>Fm3m</i>	S.B. 1-12 M.A. 7-384
Talc	$4[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$ Monoclinic ( <i>2/m</i> )	5-26 9-10	18-91 80°	9-01 2-45	3-06 1-52	Pyrophyllite ( <i>S56</i> ) <i>C2/c</i>	S.B. 3-159 M.A. 6-45
Tantalite	$4[(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6]$ Orthorhombic ( <i>mmm</i> )	14-21 5-73	5-03	3-04 1-72	2-97 1-46	Niobite ( <i>E51</i> ) <i>Pben</i>	S.B. 2-55, 337
Tapolite	$2[\text{FeTa}_2\text{O}_6]$ Tetragonal ( <i>4/mmm</i> )	4-74	9-21	3-33 1-75	2-57 1-41	Not determined <i>P4mmm</i>	M.A. 3-181
Teallite	$4[\text{PbSnS}_2]$ Orthorhombic ( <i>mmm</i> )	4-04 4-23	11-33			Tin sulphide ( <i>B20</i> ) <i>Pmcn</i>	S.B. 3-14

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Tennantite	$8[\text{Cu}_3\text{AsS}_3]$ Cube ( $\bar{4}3m$ )	10.19	2.95 1.81	Close to Blende ( $D3$ ) $I\bar{4}3m$	S.B. 1-70 M.A. 4-27
Tenorite	$4\text{CuO}$ Monoclinic ( $2/m$ )	4.05 3.41 80° 31'	2.51 1.85	Tenorite ( $D2d$ ) $C2/c$	S.B. 3-11 M.A. 6-174
Tephroite	$4[\text{Mn}_2\text{SiO}_4]$ Orthorhombic ( $nmm$ )	4.00 10.60	2.88 1.81	Olivine ( $H11$ ) $P6mm$	S.B. 1-352
Tetradymite	$\text{Bi}_2\text{Te}_2\text{S}$ Rhombohedral ( $\bar{3}m$ )	10.31	3.04 2.12	Tetradymite ( $C33$ ) $I\bar{4}3m$	S.B. 3-28 M.A. 6-38
Tetraedrite	$8[\text{Cu}_3\text{SbS}_3]$ Cube ( $\bar{4}3m$ )	10.33	4.72 2.26	Close to Blende ( $D3$ ) $I\bar{4}3m$	S.B. 1-70 M.A. 4-27
Thenardite	$8[\text{Na}_2\text{SO}_4]$ Orthorhombic ( $nmm$ )	5.85 12.29	3.00 1.84	Sodium sulphate ( $H17$ ) $Fdd\bar{2}$	S.B. 2-88 M.A. 5-181
Thermonatrite	$4[\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}]$ Orthorhombic ( $nm$ )	10.72 6.44	4.06 2.78	Sodium carbonate monohydrate ( $G70$ ) $P6_3$	S.B. 4-42 M.A. 6-413
Thomsonite	$4[\text{NaCa}_2\text{Al}_3\text{Si}_2\text{O}_{20} \cdot 6\text{H}_2\text{O}]$ Orthorhombic ( $nm$ )	13.07 13.07	5.30 2.07	Natrolite type ( $S010$ ) $Pnn$	S.B. 3-108 M.M. 23-51
Thortveitite	$2[\text{Sc}_2\text{Si}_2\text{O}_7]$ Monoclinic ( $2/m$ )	6.50 8.58	4.07 3.30	Thortveitite ( $S21$ ) $C2/m$	S.B. 2-124 M.A. 6-333
Topaz	$4[\text{Al}(\text{F}, \text{OH})_2\text{SiO}_4]$ Orthorhombic ( $nmm$ )	4.04 8.78	3.20 1.40	Topaz ( $S5$ ) $P6mm$	S.B. 2-110 M.A. 4-32
Torbernite	$2[\text{Cu}(\text{VO}_2)_2\text{P}_2\text{O}_8 \cdot 12\text{H}_2\text{O}]$ Tetragonal ( $\bar{4}/mmm$ )	7.05	2.90 1.38	Not determined $I\bar{4}/mmm$	S.B. 2-405
Tourmaline	$[(\text{NaCa}_2)(\text{Mg}_2\text{Al}_2\text{Fe})\text{B}_3\text{Si}_3\text{H}_{11}\text{O}_{33}]$ Rhombohedral ( $\bar{3}m$ )	9.50	3.48 2.50	Not determined $I\bar{4}3m$	M.A. 7-92
Tremolite	$2[\text{H}_2\text{Ca}_2\text{Mg}_2(\text{SiO}_3)_3]$ Monoclinic ( $2/m$ )	9.78 17.80	4.30 3.78	Tremolite ( $S42$ ) $I2/m$	S.B. 2-13 M.A. 4-201
Tridymite	$4[\text{SiO}_2]$ Hexagonal ( $6/mmm$ )	5.03	4.05 2.94	$\beta$ -Tridymite ( $C10$ ) $C6/mmc$	S.B. 1-171 M.A. 3-341
Tysonite	$6[(\text{Ce}, \text{La}, \text{D})\text{F}_3]$ Hexagonal ( $6/mmm$ )	7.12		Tysonite ( $D0$ ) $C6/mcm$	S.B. 2-27 M.A. 5-24



Ulexite	$2[\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}]$ Anorthic (1)	8-71 12-72 6-60	90° 15' 100° 8' 105° 7'	3-13 2-00	2-84 2-00	Not determined $P_1$	M.A. 8-217
Uilmannite	$4[\text{NiSbS}]$ Cubic (23)	5-90		4-15 2-41	2-04 1-78	Cobaltite ( $F_1$ ) $P_{2,3}$	S.B. 1-209 M.A. 8-8
Uraninite	$4[\text{UO}_2]$ Cubic ( $m3m$ )	5-47		3-11 1-02	2-70 1-03	Fluorite ( $G_1$ ) $Fm3m$	S.B. 1-148 M.A. 6-174
Uvarovite	$8[\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}]$ Cubic ( $m3m$ )	11-95		3-02 2-40	2-09 1-60	Garnet ( $S_{1,4}$ ) $Ia3d$	S.B. 1-303 M.A. 4-111
Valentinite	$4[\text{Sb}_2\text{O}_3]$ Orthorhombic ( $mmm$ )	4-92 12-16	5-42	4-10 1-80	3-09 1-52	Valentinite $P_{cen}$	S.B. 4-20 M.A. 7-85
Vanadinite	$2[\text{Pb}_3\text{Cl}(\text{VO}_4)_3]$ Hexagonal (0/m)	10-31	7-34	3-01 1-55	2-95 1-93	Apatite ( $H57,60$ ) $C6_3/m$	S.B. 2-09 M.A. 5-184, 317
Variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ Orthorhombic ( $mmm$ )	9-85 9-55	8-50	5-42 3-03	4-25 2-85	Not determined $P_{cab}$	M.A. 8-51
Vermiculite	$4[(\text{OH})_2(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al}, \text{Fe})_4\text{O}_{16} \cdot 4\text{H}_2\text{O}]$ Monoclinic ( $m$ )	5-33 9-18	28-85 80° 45'	13-1 2-37	3-54 1-53	Hendricks (1938) $C_c$	M.A. 7-397
Vivianite	$2[\text{Fe}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ Monoclinic ( $2/m$ )	10-04 13-30	4-09 75° 42'			Not determined $C2/m$	M.A. 7-259
Willemite	$6[\text{Zn}_2\text{SiO}_4]$ Rhombohedral ( $\bar{3}$ )	8-63	107° 15'	2-84 2-32	2-03 1-42	Phenakite ( $H19$ ) $R\bar{3}$	S.B. 1-356 M.A. 4-108
Witherite	$4[\text{BaCO}_3]$ Orthorhombic ( $mmm$ )	5-25 8-83	0-54	3-72 2-14	2-03 2-03	Arakonite ( $G2$ ) $P_{cmn}$	S.B. 1-295 M.A. 5-190
Wolframite	$2[(\text{Fe}, \text{Mn})\text{WO}_4]$ Monoclinic ( $2/m$ )	4-78 5-73	4-08 89° 34'	2-92 2-18	2-46 1-70	Magnesium tungstate ( $H6$ ) $P_{2/c}$	S.B. 2-85
Wolfsbergite	$4[\text{CuSbS}_2]$ Orthorhombic ( $mmm$ )	0-01 3-73	14-46	3-22 2-33	3-04 2-16	Wolfsbergite ( $F56$ ) $P_{nma}$	S.B. 3-75 M.A. 5-311
Wollastonite	$12[\text{CaSiO}_3]$ Monoclinic ( $2/m$ )	15-33 7-29	7-07 84° 35'	3-30 2-17	2-96 1-71	Wollastonite ( $S33$ ) $P_{2,1/a}$	S.B. 4-71 M.A. 6-332
Wulfenite	$4[\text{PbMoO}_4]$ Tetragonal ( $4/m$ )	5-41	12-08	3-17 1-77	2-00 1-01	Scheelite ( $H4$ ) $I4_1/a$	S.B. 1-347 S.B. 2-83
Wurtzite	$2[\text{ZnS}]$ Hexagonal ( $6mm$ )	3-84	6-28	3-12 1-03	1-91 1-24	Wurtzite ( $B4$ ) $C6mc$	S.B. 1-78 M.A. 3-20

I. Mineral.	II. Unit-cell contents and symmetry.	III. Unit-cell dimensions.	IV. Powder data.	V. Structure-type and space-group.	VI. References.
Xenotime	4[YPO <sub>4</sub> ] Tetragonal (4/mmm)	6.88 6.01		Zircon (H3) I <sub>4</sub> /amd	S.D. 1-345 M.A. 3-431
Zincoite	2[ZnO] Hexagonal (6mm)	3.22 5.20	2.81 2.46	Wurtzite (B4) C6mc	S.D. 1-78 M.A. 1-313
Zinckenite	12[PbSb <sub>2</sub> S <sub>2</sub> ] Hexagonal (6/m)	44.06 8.60		Not determined C6 <sub>3</sub> /m	M.M. 25-221
Zircon	4[ZnSiO <sub>4</sub> ] Tetragonal (4/mmm)	6.60 5.99	4.32 1.70	Zircon (H3) I <sub>4</sub> /amd	S.D. 1-345 M.A. 7-132
Zunyte	4[Al <sub>2</sub> Si <sub>2</sub> O <sub>10</sub> (OH, F) <sub>2</sub> Cl] Cubic (43m)	13.82		Zunyte (S8) F43m	S.D. 3-147 M.A. 5-325

NOTE.—Only seven space-groups in the hexagonal system are based upon a rhombohedral lattice with  $a=b=c$ ;  $\alpha=\beta=\gamma=90^\circ$ . Minerals tabulated above as rhombohedral belong to one of these space-groups.

space-groups, and powder-photograph measurements. Rare species are listed only when the structural type to which they belong is not represented by a better known mineral. Following the mineral name in column I is the repeat or atomic contents of the unit cell. For convenience this is still called the molecular formula by some authors, but actual molecular association is extremely rare amongst mineral and inorganic crystal structures. The unit-cell contents expressed in this way, as a formula, must not only represent the chemical analysis of the given mineral but must equal in weight the product of the specific gravity and the unit-cell volume measured by X-ray methods. Immediately beneath the repeat in column II are given the system of symmetry and the crystal class or point-group symmetry in parentheses. The point-group symmetry is expressed by the symbols for the necessary and sufficient combination of axes of rotation (2, 3, 4, and 6), axes of rotatory inversion ( $\bar{2}$ ,  $\bar{3}$ ,  $\bar{4}$ , and  $\bar{6}$ ) and symmetry planes ( $m$ ). A list of names formerly used for the 32 crystal classes and the corresponding symbols now used by X-ray crystallographers are tabulated separately. This list also shows how the unit cell is defined for each of the given systems of symmetry.

Unit-cell dimensions are given in Angstrom units ( $10^{-8}$  cm.) in column III and are listed so

#### LIST OF THE NAMES AND SYMBOLS OF THE THIRTY-TWO CLASSES OF CRYSTAL SYMMETRY.

System.	Name.	Symbol.
Cubic $a=b=c$ $\alpha=\beta=\gamma=90^\circ$	Ditesseral central	$m\bar{3}m$
	Ditesseral polar	$\bar{4}3m$
	Tesseral central	$m\bar{3}$
	Tesseral holoaxial	$\bar{4}3$
	Tesseral polar	$\bar{2}3$
Tetragonal $a=b\neq c$ $\alpha=\beta=\gamma=90^\circ$	Ditetragonal equatorial	$4/mmm$
	Ditetragonal alternating	$\bar{4}2m$
	Ditetragonal polar	$4mm$
	Tetragonal equatorial	$4/m$
	Tetragonal holoaxial	$\bar{4}2$
	Tetragonal polar	$\bar{4}$
	Tetragonal alternating	$\bar{4}$
Hexagonal* $a=b\neq c$ $a\wedge b=120^\circ$ $a\wedge c=b\wedge c=90^\circ$	Dihexagonal equatorial	$6/mmm$
	Dihexagonal polar	$6mm$
	Ditrigonal equatorial	$6m2$
	Hexagonal equatorial	$6/m$
	Hexagonal holoaxial	$\bar{6}2$
	Hexagonal polar	$\bar{6}$
	Trigonal equatorial	$\bar{6}$
	Ditrigonal polar	$3m$
	Dihexagonal alternating	$3m$
	Trigonal holoaxial	$\bar{3}2$
	Trigonal polar	$\bar{3}$
Orthorhombic $a\neq b\neq c$ $\alpha=\beta=\gamma=90^\circ$	Hexagonal alternating	$m$
	Didigonal equatorial	$mmm$
	Didigonal polar	$2mm$
	Didigonal holoaxial	$222$
	Digonal equatorial	$2/m$
	Planar	$m$
Monoclinic $a\neq b\neq c$ $\alpha=\gamma=90^\circ$ $\beta\neq 90^\circ$	Digonal polar	$2$
	Central	$\bar{1}$
Anorthic $a\neq b\neq c$ $\neq\beta\neq\gamma\neq 90^\circ$	Asymmetric	$1$

\*See footnote to Tables.

that the  $a$  and  $b$  dimensions fall in the same vertical column and  $c$  on the right and in line with  $a$ . Three lines are used for anorthic minerals so that  $a$  and  $\alpha$  are given on the first line,  $b$  and  $\beta$  on the second, and  $c$  and  $\gamma$  on the third. The axial ratios may be calculated from  $c/a$  for tetragonal and hexagonal minerals and from  $a/b$  and  $c/b$  for orthorhombic, monoclinic, and anorthic minerals. They will be in agreement with those obtained by measurement of the angles between crystal faces with the goniometer, or related to them by a simple multiple or sub-multiple, according to the choice of parametral plane.

The accuracy of measurement of unit-cell dimensions has greatly increased since many of the tabulated data were obtained. Investigators are also more consistently carrying out their measurements on material subjected to chemical analysis. Correlated data can then be tabulated for the end members of all isomorphous series of minerals, and the complex character of atomic replacements or solid solution in so many minerals correctly interpreted.

Column V gives the crystal-structure type. The names and symbols of the structure types are more or less arbitrary and historical, but the classification used in the "Strukturbericht" is adopted here, since it fulfils its purpose of giving a quick idea of the structure. "There is as yet no rational way of bringing the structures into a system which will correlate both the geometrical and dynamical or chemical qualities of kindred structures" (Z. Krist. 1931, 79, 513).

The symbol of the crystal-structure type consists of a letter and a number. The initial capital letter refers to the following classification into sections:  $A$ , elements;  $B$ , compounds of type  $AX$ ;  $C$ ,  $AX_2$ ;  $D$ ,  $AmX_n$ ;  $F$ ,  $Am(XYZ)_n$ ;  $G$ ,  $Am(BX_3)_n$ ;  $H$ ,  $Am(BX_2)_n$ ; and  $S$  silicates.

Beneath the name and symbol of the crystal-structure type in column V is given the Hermann-Mauguin nomenclature for the space-group. For a full description of these symbols and the 230 space-groups, see "Internationale Tabellen zur Bestimmung von Kristallstrukturen," 1935, Vol. I, pp. 12-18 and 94; and W. T. Astbury and Kathleen Yardley, "Tabulated Data for the Examination of the 230 Space-groups by homogeneous X-Rays," Proc. Roy. Soc. 1924, A, 224, 221.

Briefly, the capital letter beginning each space-group notation is one of the lattice symbols  $P$ , primitive,  $A$  centred on the (100) face,  $F$ , face-centred, etc.; next follows the symbol of the principal axis, and this may be an axis of rotation, an axis of rotatory inversion, or a screw-axis. Screw-axes and glide-planes are symmetry elements proper to a lattice and involve translations as well as the customary rotation or reflection. Screw-axis symbols are  $2_1, 3_1, 3_2, 4_1, 4_2, 4_3$ , etc., signifying by the subscript the amount of translation following a rotation, e.g.,  $6_2$  translates  $\frac{2}{6} = \frac{1}{3}$  of the cell dimension after  $\frac{2}{6}$  full turn about that direction. If there is a plane of symmetry perpendicular to the axis it follows, separated by an oblique rulo, e.g.,  $2/m$ . Then follow the secondary axes or planes to complete the space-group. Glide-planes are always represented by small letters:

$a, b, c$  for those with  $\frac{1}{2}$  translation parallel to the  $a, b, c$  axes;  $n$  or  $d$  for one with  $\frac{1}{2}$  or  $\frac{1}{4}$  translation parallel to [011], [101], or [110] (W. H. Bragg and W. L. Bragg, "The Crystalline State," London, 1933, pp. 63-88).

The reference to the page and volume of "Strukturbericht" is given in the last column, and whenever possible the reference to the relevant paper abstracted in the Mineralogical Magazine is given in the form M.A. 4-16, i.e., p. 16 of volume 4 of the Mineralogical Abstracts. Where the work has not proceeded to the complete analysis of crystal structure the abstract of the most recent paper has been cited, so that the cell dimensions quoted may be as accurate as possible.

No two substances possess the same crystal structure, so that a metrical definition of the unit of pattern of a given mineral is unique for that mineral. It is to be expected therefore that the photographic records of diffraction spectra upon which the X-ray analysis is based should themselves constitute precise identifications. The unit-cell dimensions are diagnostic, and a rotation photograph of a crystal of a known mineral about a known axis gives a two-dimensional array of spots of varying intensities, forming a standard for identification. Powder photographs are more widely used for this purpose, and extend identification by X-rays to those substances which are crystalline but which have grown in amorphous masses possessing no crystal faces and often of very small particle-size. The spacings and relative intensities of powder photographs of about 250 minerals have been listed by A. K. Boldyrev *et al.* as "X-Ray Determinative Tables for Minerals," Parts I and II (Annales de l'Institut des Mines à Leningrad, 1938, 11, pt. 2; 1939, 12, pt. 1). J. D. Hanawalt and others also listed powder data for a thousand chemical compounds, mostly artificial, claiming that a knowledge of the spacings of the three most intense lines and their relative intensities sufficed in most instances for identification (Ind. Eng. Chem. [Anal.], 1938, 10, 457). G. A. Harcourt has extended Hanawalt's data by the spacings for 162 ore-minerals, a particularly useful aid to the X-ray identification of ores (Amer. Min. 1912, 27, 63). Hanawalt's data have been made up into a card-index file by the American Society for Testing Materials and the American Society for X-Ray and Electron Diffraction. Data for many more minerals and compounds are being collected in this country under the auspices of the X-Ray Analysis Group of the Institute of Physics, and will form an appendix to the American Card Index already published. Four strong line-spacings of as many minerals listed in the Tables as possible are given in column IV, abstracted from both the Russian and American lists. They serve as a guide to mineralogists using the X-ray powder method and would need confirmation by the comparison of the complete photograph with a standard.

F. A. B.

**MINERALS, GEOCHEMISTRY OF.**  
The geochemistry of minerals comprises the description and understanding of the chemical and physical conditions which are necessary for

the formation and transformation of the various minerals and mineral assemblages in rocks, ores, and other mineral deposits, likewise in soils. The chemical conditions of primary importance for the formation of minerals are the presence and the proportions of the various chemical constituents of the minerals. Therefore, the first and most important object of geochemistry is the study of the relative amounts and distribution of the chemical elements in relation to the astrophysical prehistory and geological history of the earth.

The relative abundance of the chemical elements in the universe can be studied by astrophysical spectrum analysis (emission and absorption spectra) of stellar atmospheres, nebulae, and interstellar matter, by chemical and physical analysis of meteorites, and by comparison with analytical results obtained from accessible terrestrial matter.

The general result of such investigations is as follows: the abundance of the chemical elements follows certain rules which are correlated with important properties of the atomic nuclei. If the elements are arranged according to increasing nuclear charge, starting with the neutron, then the first stable element, hydrogen, is by far the most abundant, the atomic frequency of hydrogen being much in excess of the combined frequency of all other elements (Russell, Science, 1941, 94, 375). Then comes helium, the most important product of nuclear condensation, followed by three elements which are comparatively rare in all parts of the universe, viz. lithium, beryllium, and boron, the nuclei of which at stellar temperatures are unstable against collisions with protons. From oxygen to uranium the cosmic abundance of the elements seems, in general, to follow the rule that abundance decreases with increasing nuclear charge, so that the abundance of oxygen (nuclear charge 8) is about 100 million times greater than the abundance of uranium (nuclear charge 92). Important exceptions to the rule are the relatively great abundance of iron and the neighbouring elements (nuclear charge 25-28). Another general rule, discovered by Oddo and Harkins, states that elements with odd nuclear charges are usually less abundant than the neighbouring elements with even nuclear charges [for instance, La (57) is less abundant than Ba (56) and Ce (58)].

If the atomic species, not the chemical elements, are arranged according to mass numbers, it is found that in nearly every case the abundance of atomic species with odd mass-numbers is less than the abundance of neighbouring atomic species with even mass-numbers—for instance,  $^{138}_{56}\text{Ba}$ : $^{139}_{57}\text{La}$ : $^{140}_{58}\text{Ce}$ =3:1:2.3. All these rules concerning the cosmic proportions of atomic species without doubt reflect nuclear stability properties involved in the evolution and survival of atomic species (Goldschmidt, Skrifter Norske Videnskaps-Akad. i. Oslo, I, Mat. Natur. Klasse, 1937, No. 4).

The average composition of matter in the crust of the earth (atmosphere, hydrosphere, and uppermost part of the lithosphere) is, however, different in many respects from the average

composition of cosmic matter, owing to processes of selective separation during the astrophysical and geological prehistory of the earth (Goldschmidt, Videnskapsselskapets-Skrifter, I, Mat. Naturv. Klasse, Kristiania, 1923, No. 3; Proc. Roy. Inst. 1929; J.C.S. 1937, 655).

Since the earth, like any other planet, has presumably been formed by condensation of gaseous matter, either in one single step or by condensation to smaller bodies which have since coalesced, it is necessary to consider the behaviour of matter and the distribution of elements during such condensation. The most volatile elements, and elements forming very volatile compounds, will remain in a primordial atmosphere, as, for instance, the inert gases, nitrogen, and oxides of carbon and of hydrogen. These elements are called atmophil elements. How much of the atmophil elements can be retained in the primordial atmosphere depends on the size of the planet (field of gravitation) and temperature. Possibly the present atmosphere and hydrosphere of the earth are essentially products of secondary degassing.

Other elements which form non-volatile oxides will combine with oxygen to form a fused slag, consisting essentially of compounds of those elements which have greatest free energy of oxidation per unit of valency, such as silicon, aluminium, magnesium, calcium, and the alkali metals. Such elements, including oxygen, are called lithophil elements.

Since iron is by far the dominant *heavy metal*, the limit for oxidation processes is given by the free energy of oxidation of iron, and those metals which have a free energy of oxidation less than that of iron per unit of valency are left essentially in an unoxidised state, forming alloys and compounds with metallic iron dominating. These are the siderophil elements, and include nickel, cobalt, germanium, gold, and the metals of the palladium and the platinum groups. Therefore, gold and platinum, for instance, are extremely "dilute" in the silicate magmas of the earth's crust, but are found in much larger concentrations in the iron-nickel alloys of meteorites and, probably, also in nickel-iron alloys in the innermost parts of the earth (see Goldschmidt, Soil Sci. 1945, 60, 1).

A fourth group of elements, the chalcophil elements, are characterised by a strong affinity for sulphur and arsenic, and are found in the sulphide phases of meteoritic and sulphide ores of terrestrial origin. The grouping of chalcophil elements is rather different in the sulphides of meteorites and in terrestrial ore-bodies, because in the meteorites the total amount of oxygen and sulphur is usually not sufficient to saturate all metal valencies, so that unsaturated free metals are left. Because of the oxygen deficiency in nearly all meteorites, we observe sulphides of a number of elements which in terrestrial matter usually or exclusively combine with oxygen, such as calcium, manganese, chromium, and vanadium (Goldschmidt and Peters, Nachr. Ges. Wiss. Göttingen, math.-phys. Kl. 1933, 278). In terrestrial materials the oxygen and sulphur have to compete for the heavy metal atoms, usually in the absence of an excess of uncom-

bined metals. Thus the chalcophil metals in ore deposits of the earth's crust follow another grouping, giving an illustrative example of the importance of the *oxidation-reduction potential* in the geochemistry of minerals.

Another reason for the great difference between meteoritic and terrestrial minerals is the abundance of water in terrestrial materials.

Table I contains the classification of elements according to their distribution in the primordial atmosphere, the nickel-iron core, the slag crust, and the sulphide phases. The elements concentrated in living organisms, the *biophil* elements, are tabulated as a fifth group. The concentration of the biophil elements, however, belongs to distinctly later periods in the geochemical evolution of the earth.

It is probable that the bulk of siderophil and chalcophil elements in terrestrial matter are concentrated in the interior of the earth; in the accessible crust of our planet we find that most minerals consist predominantly of lithophil elements.

The average composition of the uppermost parts of the lithosphere, however, does not correspond exactly with the average amounts of all terrestrial lithophil matter, but is much modified by *fractional crystallisation* in such a manner that in the gravitation field of the earth crystallises and heavy magmas have a tendency to migrate towards the centre, while light minerals, light magmas, and light aqueous mother liquors have a tendency to migrate towards the surface of the earth.

TABLE I.—GEOCHEMICAL CLASSIFICATION OF THE ELEMENTS, ACCORDING TO DISTRIBUTION BETWEEN IRON, SULPHIDES, SILICATES, ATMOSPHERE, AND ORGANISMS.

Iron, siderophil.	Sulphide, chalcophil.		Silicates, lithophil.	Gases, atmosph.	Organisms, biophil.
	In meteorites.	Terrestrial.			
Fe, Ni, Co, P, (As), C, Ru, Rh, Pd, Os, Ir, Pt, Au, Ge, Sn, Mo, (W), (Nb), Ta, (Se), (Te)	S, Se, (Te?), P, As, (Sb), (Ti), V, Cr, Mn, Fe, Cu, Ag, Zn, Cd, (Ca)	S, Se, Te, As, Sb, Bi, (Ge), (Sn), Pb, Ga, In, Tl, Zn, Cd, Hg, Cu, Ag, (Au), Ni, Pd, (Pt), Cd, (Rh, Ir), Fe, Ru, (Os)	O, (S), (P), (H), Si, Ti, Zr, Hf, Th, (Sn), F, Cl, Br, I, B, Al, (Ga), Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, (Fe), V, Cr, Mn, (Ni), (Co), Nb, Ta, W, U, (C)	H, N, C, (O), Cl, Br, I, He, Ne, A, Kr, X	C, H, O, N, P, S, Cl, (Br), I, (B), (Ca, Mg, K, Na), (V, Mn, Fe, Cu)

In general, most of the earlier products of crystallisation of silicate magmas are heavier than the average magma. This also holds for the sulphides of iron and other heavy metals (nickel, copper) which are separated by liquation as liquid sulphide droplets.

Many of the residual magmas during the process of fractional crystallisation (granodiorites, granites, syenites, nephelite-syenites) have a low specific gravity and tend to rise. The same also holds for such mother-liquors of silicate magmas as give rise to pegmatites and to hydrothermal ore deposits.

The fate of the different elements in mineral formation connected with the crystallisation of magmas is, therefore, closely related to the general laws regulating the entrance of atoms or ions into the crystal lattices of minerals. The structure of a crystal is dependent on three factors—the proportions of the constituent particles (as defined by chemical formulae), the ratios of the sizes of these particles, and their polarisation properties. Isomorphous replacement or exchange of particles (atoms, ions, or

radicals) can take place when there is a sufficient degree of similarity in size and in polarisation properties. In particular, it has been found that crystal lattices can admit particles if the difference in radii does not exceed about 15% of the smaller radius. For any understanding and prediction of isomorphous substitution it is, therefore, necessary to have information concerning the radii of atoms or ions. Tables IIa and IIb contain *ionic radii* such as are commonly used. The one set (G.) are empirical data due to Goldschmidt (Trans. Faraday Soc. 1929, 25, 253), the list being first given in 1926; the other set (P.) was calculated semi-empirically by L. Pauling in 1927 ("Probleme der modernen Physik," Leipzig, 1928, p. 17). Another semi-empirical set has been published by Zachariasen (Z. Krist. 1931, 80, 137), and a calculation on the basis of wave mechanics has been given by Jensen, Meyer-Gossler, and Rohde (Z. Physik, 1938, 110, 277).

These data apply to the structures of ionic crystals. In most of the minerals belonging to the classes of oxides, halides, silicates, and other

TABLE IIa.—THE EMPIRICAL IONIO RADII (GOLDSCHMIDT, 1926), AND SEMI-EMPIRICAL IONIO RADII (PAULING, 1927), BOTH FOR CO-ORDINATION NUMBER 6.

Goldschmidt. Pauling	1 <sup>+</sup> H	0 He	1 <sup>+</sup> Li	2 <sup>+</sup> Be	3 <sup>+</sup> B	4 <sup>+</sup> C max. 0.2 0.15	5 <sup>+</sup> N max. 0.1-0.2 0.11	0 <sup>+</sup> S 0.34 0.20	1 <sup>+</sup> Cu — 0.00	2 <sup>+</sup> Zn 0.83 0.74	3 <sup>+</sup> Ga 0.82 0.62	4 <sup>+</sup> Ge 0.44 0.53	0 <sup>+</sup> Se 0.3-0.4 0.42
G. . . . .	1.27 2.08	ca. 1.22 —	0.78 0.60	0.34 0.31	— 0.20	0.15	0.11	0.34 0.20	— 0.00	0.83 0.74	0.82 0.62	0.44 0.53	0.3-0.4 0.42
P. . . . .	1.33* 1.36	ca. 1.52 —	0.08 0.05	0.78 0.05	0.57 0.50	0.30 0.41	0.34 0.34	0.34 0.20	— 0.00	1.03 0.97	0.82 0.62	0.44 0.53	0.3-0.4 0.42
G. . . . .	1.74 1.84	ca. 1.02 —	1.33 1.33	1.00 0.00	0.83 0.81	0.64 0.68	0.4 0.50	0.3-0.4 0.52	— 0.00	1.03 0.97	0.82 0.62	0.44 0.53	0.3-0.4 0.42
P. . . . .	1.81 1.81	ca. 2.1 —	1.48 1.48	1.27 1.13	1.00 0.03	0.87 0.80	0.00 0.70	— —	— 1.37	1.03 0.97	0.82 0.62	0.44 0.53	0.3-0.4 0.42
G. . . . .	1.01 1.08	ca. 2.3 —	1.05 1.09	1.43 1.35	1.22 1.15	1.02 1.01	— —	— —	— 1.37	1.12 1.10	1.05 0.65	0.84 0.84	0.3-0.4 0.42
P. . . . .	2.21 2.21	ca. 2.3 —	1.05 1.09	1.43 1.35	1.22 1.15	1.02 1.01	— —	— —	— 1.37	1.12 1.10	1.05 0.65	0.84 0.84	0.3-0.4 0.42

\* The radii for univalent F (1.33) and bivalent O (1.32) are due to Wasastjerna.

† From "Geochemische Verteilungsgesetze," Part VIII, printed 31 January, 1927.

TABLE IIb.—SOME EMPIRICAL RADII, AFTER GOLDSCHMIDT AND PAULING.

G.	1 <sup>+</sup> NH <sub>4</sub> 1.43	1 <sup>+</sup> Ti 1.40	2 <sup>+</sup> Mn 0.81	2 <sup>+</sup> Fe 0.83	2 <sup>+</sup> Ni 0.78	2 <sup>+</sup> Pb 1.32	3 <sup>+</sup> V 0.05	3 <sup>+</sup> Cr 0.04	3 <sup>+</sup> Mn —	3 <sup>+</sup> Fe 0.07	3 <sup>+</sup> Rh 0.08	3 <sup>+</sup> Lu 0.09
P.	—	1.40 1.40	0.80	0.75	0.69	1.21	—	—	—	—	—	—
G.	1.22	1.18	1.10	1.15	1.13	1.12	1.09	1.07	1.05	1.03	1.01	1.00
P.	—	—	—	—	—	—	—	—	—	—	—	—
G.	0.01 0.50	0.52 0.50	0.60 0.07	0.68 0.60	1.05 0.07	0.63 0.63	0.00 0.04	0.80 0.81	1.00 0.02	0.80 —	1.10 1.02	1.00 0.09
P.	—	—	—	—	—	—	—	—	—	—	—	—

\* The data for the trivalent cations of Ti, V, Cr, Mn, Fe, and Rh are modified according to the relative radii found by Zachariasen, Skr. Math.-Naturv. Kl. 1928, 4, 118. Minor corrections for trivalent Eu, Er, Tm, and Yb have also been made (see Bommer, Z. anorg. Chem. 1930, 211, 273).

salts of oxy-acids, such as carbonates, sulphates, and phosphates, the metallic constituents are present as ions, and the radii corresponding with the respective degrees of ionisation (for instance, the ions of divalent or of trivalent iron) are the distinctive factor which decides if any such ion can, or cannot, enter a certain crystal structure, the growing crystals acting as nets or sieves which retain particles fitting into their structural dimensions. The simplest case of such substitution is when ions of the same or nearly the same size, and of identical charge, are concerned, such as replacement of  $Mg^{2+}$ , radius 0.78 Å., by nickel with the same charge and size, or univalent positive potassium ( $r=1.33$  Å.) by rubidium ( $r=1.49$  Å.). Thus, the crystal of potash feldspar can accommodate rubidium ions instead of potassium, but cannot accommodate lithium ions ( $r=0.78$  Å.), and only to a very limited extent can it take up cesium ions ( $r=1.65$  Å.). Therefore no separate magmatic rubidium mineral has yet been discovered, whereas such a cesium mineral (*pollucite*, v. Vol. II, 195c) does exist (cf. Ahrens, Amer. Min. 1945, 30, 616).

The ability of crystals to accommodate ions of somewhat different sizes is greater at elevated temperatures than at lower temperatures, owing to the increase in thermal displacement of individual particles at high temperatures.

The simplest case of isomorphous substitution has just been considered, that which takes place between ions of similar size and the same charge. The extreme case of such similarity is attained when ions of the same type, the same valency, and nearly the same size substitute each other, as in the following pairs:

Ion $r(\text{Å.})$	$3+$	$3+$	$3+$	$3+$	$4+$	$4+$	$5+$	$5+$
	Al	Ga	Y	Ho	Zr	Hf	Nb	Ta
	0.57	0.62	1.06	1.05	0.87	0.86	0.69	0.63

In such cases not only the structural dimensions but also the chemical properties are very nearly alike, so that the rarer element of the pair (e.g., Ga) is hidden or "camouflaged" by the more common element (i.e., Al).

The similarity of ionic size in the pairs Y-Ho, Zr-Hf, Nb-Ta is caused by the lanthanide contraction, the effect of the filling of the  $N$  shells by 14 electrons in the sequence of the rare-earth elements ("lanthanides") from  ${}_{57}\text{La}$  to  ${}_{72}\text{Hf}$  (Goldschmidt, Barth, and Lunde, Skifter Norske Videnskaps-Akad. Oslo, I, Mat. Naturv. Klasse, 1925, No. 7; Von Hevesy, Z. anorg. Chem. 1925, 147, 228; Danske Vidensk. Selsk. Math.-fys. Medd., VI, 1925, No. 7).

Many very interesting examples of assemblages of trivalent ions of similar size are furnished by the minerals of the rare-earth elements, minerals which contain compounds either of all existing elements from  ${}_{57}\text{La}$  to  ${}_{62}\text{Sm}$  (cerium group), for instance, *monazite* ( $\text{CePO}_4$ ) (v. Vol. II, 512b), or of the series  ${}_{63}\text{Gd}$  to  ${}_{71}\text{Lu}$  (yttrium group), associated with  ${}_{89}\text{Y}$  in *xenotime* ( $\text{YPO}_4$ ) (v. Vol. II, 512c) (Goldschmidt and Thomassen, Videnskapsselsk. Skifter, I, Mat. Naturv. Klasse, Kristiania, 1924, No. 5; Goldschmidt, *ibid.*

1937, No. 4). In some cases yttrium and the whole series of rare-earth elements from La to Lu are associated in the same minerals, e.g., *ytrofluorite* and many *apatites* (v. Vol. I, 449c) ("complete" assemblages).

A special case is the association of scandium with the elements ytterbium and lutecium, likewise in consequence of ionic sizes, in the mineral *thortveitite* (v. Vol. V, 524c).

Europium is not usually concentrated to any considerable extent in minerals of trivalent rare earths, as it enters certain feldspars and other minerals in the bivalent state, with an ionic radius nearly equal to that of potassium, strontium, or lead.

In many cases it is observed that isomorphous substitution is not limited to pairs of atoms or ions with the same valency or charge, but extends to pairs of elements with similar radii but different valencies or ionic charges. Thus sodium ( $r=0.98$  Å.) can be substituted by calcium ( $r=1.06$  Å.), calcium by trivalent yttrium ( $r=1.06$  Å.), and trivalent yttrium by quadrivalent thorium ( $r=1.10$  Å.).

If an ion of different charge or an atom of different valency enters in place of one of the proper constituents of the crystal, then some kind of compensation must take place to secure the electroneutrality of the lattice as a whole. This takes place in different ways. For example, in *cassiterite* ( $\text{SnO}_2$ ) (v. Vol. II, 419b), three tin ions can be substituted by one of ferrous iron and two of niobium, or two of tin can be replaced by one of scandium and one of niobium. In many cases of such replacements, the average radii of the substituting cations are very close to the radii of the cations of the host crystal (Goldschmidt, Chem. Products, 1944, 7, 33). The compensation can also be brought about by substitution with suitable anions of different valency, e.g., in *monazite*,  $\text{CePO}_4$ , trivalent Ce can be replaced by Th, the  $\text{PO}_4$  being replaced correspondingly by  $\text{SiO}_4$ . Well-known examples are furnished in the crystallographical relationships between sodium feldspar and calcium feldspar, or between potassium feldspar and barium feldspar (v. Vol. V, 1a). In *fluor-spar*,  $\text{CaF}_2$  (v. Vol. V, 283a), bivalent calcium ions can be substituted by trivalent yttrium, the valency balance being maintained by accommodating extra fluorine ions in the fluor-spar lattice. In other cases the balance of electrical charges or of valencies is maintained by leaving certain lattice positions empty. An example of this can be given from the iron sulphides of the troilite-pyrrhotite family, where the entrance of some ferric iron, together with the dominating divalent iron, is compensated by the occurrence of a corresponding number of "empty" iron positions in the lattice, making the formula  $\text{Fe}_{(n-1)}\text{S}_n$ , where  $n$  depends upon the number of trivalent iron ions.

The knowledge of ionic or atomic radii not only permits the prediction of crystal structures and the possibility of isomorphous substitutions in crystals, but also makes possible a prediction of the sequence of entrance of substituting elements. In so far as the bonding forces are strictly or dominantly of an electrostatic nature, this sequence is essentially that of the electro-



static forces between the ions, being inversely proportional to the square of interionic distance and directly proportional to the product of the charges of opposite signs. In the case of the same charge, magnesium ( $r=0.78 \text{ \AA.}$ ), for instance, enters before bivalent iron ( $r=0.83 \text{ \AA.}$ ), and potassium before rubidium. In the case of difference in ionic charge, the higher-charged ion enters in preference to the lower-charged ion, so that trivalent scandium enters ionic silicates of magnesium and of bivalent iron in preference to these bivalent ions (the scandium is "captured" in pyroxenes of gabbro rocks) (Goldschmidt and Peters, *Nachr. Ges. Wiss. Göttingen*, IV, 1931, 257), while univalent lithium enters the magnesium-ferrous minerals mainly at that late stage of crystallisation when the supply of bivalent ions is nearly exhausted ("admittance" of lithium into the biotites of granite and syenite rocks) (Strock, *Nachr. Ges. Wiss. Göttingen*, IV, 1936, 171).

It is thus realised that the sequence of the entrance of ions of different size and different electrical charge into crystal lattices depends upon the strength of the bonding forces between the lattice and the ion under consideration, the strength of the bonding forces being indicated by the ionic charges and by the reciprocals of the radii. Of course, the actual bonding forces are never exclusively of an electrostatic nature; there is always a more or less important contribution by Van der Waals forces, and very often also by valency forces (for instance, bonding by an electron pair). Such valency forces are in part responsible for the strong bonding of such elements as chromium and nickel in certain rock-forming minerals. In fact the particle radii which are observed in actual crystals are an indication of the sum of the operative bonding forces.

The fractional crystallisation of igneous silicate magmas is, to a very high degree, controlled by the strength of bonding of the atoms (or ions) in crystal lattices, the minerals of highest crystal energy generally being the first to separate from the liquid state. This, of course, applies not only to the entrance of such rare elements as scandium and lithium into the minerals of more common elements, but also to a high degree regulates the sequence of crystallisation of these common minerals. Therefore, the silicates of magnesium generally crystallise before the aluminosilicates of calcium and the alkali metals, and magnesium enters the isomorphous mixtures in advance of bivalent iron, which again in its turn precedes bivalent manganese; lime feldspar precedes the sodium feldspar in their isomorphous mixtures, while potassium is concentrated in the last silicate fractions, together with hydroxyl and the univalent anions of the halogens. With decreasing temperatures the formation of more complex silicate and aluminosilicate anions is favoured, in comparison with the simple orthosilicate anions.

The fractional crystallisation of silicate magmas, starting with basic olivine-gabbros, passing through granites and granodiorites and ending with more or less aqueous mother-liquors giving rise to pegmatites (*v. Vol. VI, 126b*), covers an extensive interval of tempera-

ture, probably ranging in the main from about  $1,400^\circ$  down to about  $500^\circ\text{C.}$  or even less. Still lower is the temperature range of most pneumatolytic or even hydrothermal formations of epimagmatic minerals. An important phenomenon in connection with the decrease in temperature in the process of fractional crystallisation of magmas and epimagmatic vapours and liquid phases is the decrease in the ability to accommodate foreign particles in the crystal lattices involved (Bray, *Bull. Geol. Soc. Amer.* 1942, 53, 765). Through this effect, the residual mother-liquors not only collect elements which could not enter the common minerals because of the unusual size of their particles (relatively small particles such as beryllium and boron, or relatively large particles such as caesium, barium, rare-earth metals, thorium, and uranium), but at low temperatures they may even leach some rare elements from already crystallised minerals such as feldspars or apatite. The feldspars of granites and pegmatites, being formed at lower temperatures, usually contain only relatively small amounts of most of the rare elements, except rubidium, some caesium, univalent thallium, and trivalent gallium, as compared with feldspars and apatites from basic magmas which have crystallised at higher temperatures. This is one of the reasons why in granites, syenites, and their pegmatites *separate* minerals are found of many groups of rare elements, such as lithium, beryllium, and boron, rare-earth metals, tantalum and niobium, zirconium and hafnium, and thorium and uranium. In part, these rare elements are concentrated in the mother liquors by the process of fractional crystallisation, and in part they are released from earlier crystallisation products by the decrease in temperature which makes them less soluble in isomorphous mixtures. It is possible to distinguish elements which are generally concentrated in early fractions of the sequence of crystallisation of magmatic rocks (for instance, chromium, nickel, magnesium) from elements which are concentrated in the late products of crystallisation from their parent magmatic solutions, and gases; Table III furnishes some examples.

A most important chapter in the geochemistry of minerals relates to the genetic relationships of sulphide, arsenide, and thio-salt minerals, such as pyrite ( $\text{FeS}_2$ ), pyrrhotite ( $\text{Fe}_{(n-1)}\text{S}_n$ ), arsenopyrite ( $\text{FeAsS}$ ), and bournonite ( $\text{CuPbSbS}_3$ , *v. Vol. II, 53d*). These minerals, with relatively few exceptions, have a metallic lustre, and also behave similarly to metals with regard to electrical conductivity. In addition their components are not in the same ionic state as, for example, in most oxides or oxy-salts. The structural relationships are therefore not determined by the usual ionic radii, but by set of radii which have been called "atomic" or "metallic," or by "tetrahedral" or "octahedral" radii with regard to the co-ordination number. Such radii have been proposed by Goldschmidt, by Huggins, and by Pauling (Goldschmidt, *Trans. Faraday Soc.* 1929, 25: 253; L. Pauling, "The Nature of the Chemical Bond," Ithaca and London, 1942). Geochemical and isomorphic relationships in these minerals seem to be determined by such radii in much the



TABLE III.—TYPICAL ELEMENTS AND IONS FROM MOTHER LIQUORS OF SILICATE MAGMAS.

Pegmatites.	Mineral deposits from magmatic gases.	Hydrothermal mineral deposits.
Li, (Cs)	Li	Ag, Au
Be, (Mn)	Cu	Zn, Pb, Cu, Ba, (Sr), Mn
B Sc, Y, La, Ce, Pr, Nd, Sm Eu, Gd, Tb. Dy, Ho Er, Tu, Tb, Lu	B Sc, As	(B) As, Sb, Bi
Ti, Zr, Ce, Hf, Th	Sn	
Nb, Ta, (P)	P, (Nb), Ta	
Mo, (W), U	Mo, W	(Mo), U
F, Cl, OH CO <sub>3</sub>	F, Cl, OH CO <sub>3</sub>	F, Cl, OH CO <sub>3</sub>
(S)	S	S, Se, Te

same manner as "ionic" minerals are determined by "ionic" radii. Among such relationships may be mentioned the close similarity between sulphur and arsenic particles in these types of minerals, or the crystal-chemical relationships of many sulphides, arsenides, and antimonides of the elements of the iron and platinum groups, such as FeS<sub>2</sub>, NiS<sub>2</sub>, NiSbS, OsS<sub>2</sub>, PtAs<sub>2</sub>, and many synthetic compounds of similar types. The crystallisation of minerals in deposits of sulphide ores and related minerals connected with igneous rocks covers a wide temperature range, from perhaps 1,000°C. in the case of the pyrrhotite-pentlandite-nickel deposits, connected with peridotites and norites, to the low-temperature hydrothermal deposits formed at 100°C. or less, including, for instance, mercury sulphides from hot springs. Other important types of metallic ores connected with igneous rocks are pneumatolytic deposits of cassiterite (SnO<sub>2</sub>), often associated with tungsten, arsenic, lithium, boron, and fluorine compounds. Among the deposits of ores and useful minerals associated with igneous rocks, mention can be made of hydrothermal gold and silver ores, magmatic iron and titanium ores such as magnetite (*v.* Vol. VII, 462a), ilmenite (*v.* Vol. VI, 414d), and the (rare) apatite-nephelinite rocks.

The sequence of mineral assemblages connected with igneous rocks, from the high-temperature magmatic minerals to the last low-temperature products of magmatic gases and aqueous solutions, furnishes a multitude of examples of the dependence of mineral formation

on the properties of atoms and ions, the subject of geochemistry.

Not less important, but in many respects not yet so fully investigated, is the next part of the geochemical cycle of matter, comprising the processes of weathering, erosion, and sedimentation, including the formation and development of soils. The difficulties of investigation are here very much greater than with the mineral assemblages of the igneous sequence, because the products of weathering and the soils include many crypto-crystalline and colloidal minerals of as yet uncertain constitution and relationships.

The processes of weathering take place mainly through the action of the atmosphere (and, in part, the hydrosphere) on rocks and minerals. The active agents are essentially the free oxygen and carbon dioxide in the atmosphere or dissolved in the hydrosphere, the hydroxonium, bicarbonate, and hydroxyl ions of water and aqueous solutions, and the water dipoles themselves. In very many cases biogeochemical processes are involved in weathering and in the formation of soils and sediments (W. Vernadsky, "Géochimie," Paris, 1923; "La Biosphère," Paris, 1926). The processes of weathering and sedimentation in general represent a gigantic process of chemical analysis which is in continuous operation at and near the surface of the earth's crust, forming the material for sediments and for soils, as outlined in the following scheme, which contains a few examples of the sedimentary sequence. Of course, the operative processes in making sediments depend very much on climatic conditions, especially temperature and available moisture. The influence of climate is shown, for instance, in the correlation of evaporation products with dry climates, and by the frequent correlation of bauxite formation with moist tropical conditions.

TABLE IV.—CHEMICAL SUCCESSION OF SEDIMENTS.

Processes.	Examples.
1. Insoluble residua.	Sandstone, with quartz and zircon.
2. Hydrolysis . . .	Bauxite, clay.
3. Oxidation . . .	Limonite, psilomelane.
4. Reduction . . .	Coal, oil, sedimentary sulphides, sulphur.
5. Carbonation . . .	Limestone, dolomite.
6. Evaporation . . .	Chlorides, sulphates, borates.

A number of coarse-grained sedimentary rocks, such as arkoses, greywackes, tillites, and many conglomerates, are derived from their parent materials mainly by mechanical disintegration and erosion, without much chemical weathering and differentiation.

The most important physico-chemical property for the sedimentary sequence of rocks and mineral assemblages has been found to be the ionic potential  $Z/r$ , where  $Z$  is the ionic charge (for instance, 2 in a bivalent ion) and  $r$  is the ionic radius. This ionic potential measures the electrical field-strength at the surface of the ion involved and in most cases controls the behaviour of the ion towards dipoles in solvents,

especially towards hydroxyl in the sedimentary cycle. For ions of the inert-gas types, the following numerical rules can be applied. If the potential is less than about 4, soluble cations are formed at pH about 7-8, as in the case of alkalis and alkaline earths (except beryllium); if between 4 and 12 rather insoluble hydroxides or complex hydrolysates are obtained, such as hydrated aluminosilicates, as in the case of beryllium, aluminium, and titanium; and if the ionic potential (of the hypothetical cation) is in excess of about 12, it forms valency bonds with oxygen and hydroxyl to form the central atom of soluble complex oxy-acids, such as boric, sulphuric, nitric, and phosphoric acids.

A simple diagram (Fig. 1) may illustrate the distribution of such elements in the sedimentary cycle (Goldschmidt, *Geol. Föreningens Stockholm Förh.* 1934, 56, 385).

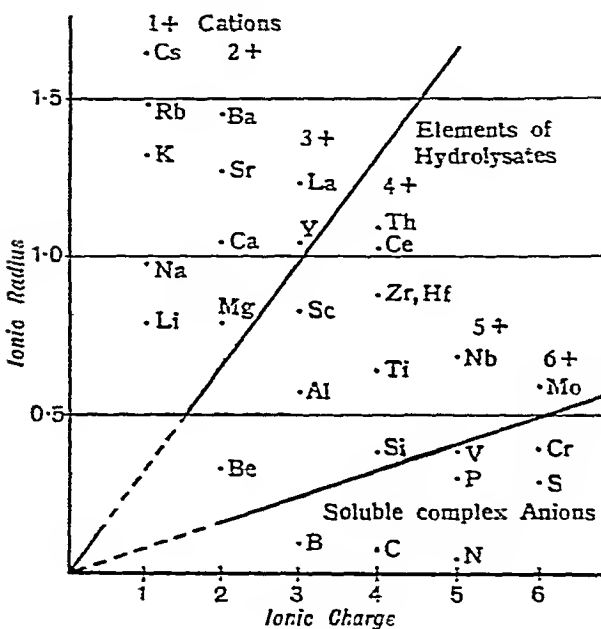


FIG. 1.

The chemical separations and concentrations of elements throughout the sedimentary cycle are of very great practical importance. Among the residual sediments we find quartz sands, sandstones, and quartzites, e.g., gneisses, as well as the auriferous quartz conglomerates of the Witwatersrand; the hydrolysates furnish refractory clays, kaolinites, and bauxites; the oxides comprise the most important iron and manganese ores; the products of reduction comprise sulphur, sedimentary pyrites, oil, coal, and oil shales; the carbonation products comprise limestone and dolomites; the evaporation products, all the salt deposits from sea water and inland lakes, including sedimentary chlorides, borates, sulphates, and nitrates. The overwhelming bulk of the annual production of mineral wealth is derived from the sedimentary cycle. In addition, nearly all of the phosphate deposits are derived from this cycle by several processes of natural concentration of calcium

phosphate from the very small percentage of phosphates in the water of the ocean.

The distribution of rare elements in sediments generally follows the order of ionic potentials, modified by adsorption phenomena which in many cases fix soluble ions to hydrolysate and oxidate sediments, thereby greatly reducing the amounts of such poisonous substances as arsenic, copper, lead, and selenium which would otherwise have concentrated in the water of the ocean (*cf.* Ahrens, *S. African J. Sci.* 1945, 41, 152). The retention also of a large amount of potassium (including rubidium and caesium) in hydrolysate sediments and in soils is a process of very great biochemical importance as a factor of soil fertility.

Of still greater economic importance, however, is the formation of soils, especially those of agricultural and sylvicultural value. The processes of weathering and leaching primarily concerned are closely related to those processes in sediment formation which result in residual sediments, hydrolytic products and, in part, the products of oxidation and reduction, under various climatic conditions. The minerals and mineral assemblages in soils are therefore very closely akin in most cases to the corresponding assemblages in sedimentary rocks. Relatively coarse granular sands and silts are found as constituents of soil, representing the least soluble residual constituents of weathered rocks, for example quartz, alkaline feldspars, magnetite, ilmenite, and zircon (*Hart, J. Agric. Sci.* 1941, 31, 438; 1942, 32, 373). These residual minerals, together with a greater or lesser amount of such typical hydrolysates as *montmorillonite* (*r.* Vol. III, 196a; V, 381d), *hydromica*, *chlorites*, *kaolinite* (*r.* Vol. VII, 95a; III, 196a), *hydrargillite* (*r.* Vol. V, 532a), and amorphous hydroxides and hydrosilicates of aluminium, as well as oxides of iron and manganese, constitute the bulk of the inorganic material of nearly all soils, apart from subordinate amounts of calcium and

magnesium carbonates, and in a few cases evaporation products such as chlorides or sulphates and bicarbonates, generally of sodium (in alkaline soils). The finest fractions of soils (the "clay" fractions), especially, seem to correspond closely to hydrolysate sediments.

A most important constituent of soils is water, usually very much in excess of the percentage of water in consolidated sediments. The "bound" water in soils seems to derive many of its essential properties from its association with layer-lattice hydrolysate minerals, either entering into their structures or being oriented (polarised) at their surfaces (*see* Hendricks and Jefferson, *Amer. Min.* 1938, 23, 836).

One very marked feature in most soils is the differentiation or "zoning" of the profile, resulting from translocation of organic matter, sesquioxides, etc., by percolating solutions, the production and decay of organic matter, different conditions of oxidation and reduction, differ-

ences in pH, and corresponding differences in leaching and accumulation of the various constituents.

The nature of the mineral assemblages characteristic of the finest materials in the different types of soils can only be given in broad outline as yet. The available data suggest that climatic conditions determine to a large extent the nature of the end products in mature soils: thus, the eluvial horizons of the soils of moist temperature and tropical zones are characterised by the predominance of clays of the kaolinite type, whilst those of the semi-arid and arid zones contain for the most part members of the montmorillonite group (see Table V, which is based on Hardy and Rodrigues, *Soil Science*, 1939, 48, 361; Hendricks and Alexander, *ibid.*, p. 257; Nagelschmidt, Desai, and Muir, *J. Agric. Sci.* 1940, 30, 639; Sedletzky, *Pedology*, 1942, Pt. 3/4, 61). The Red and Black Earths provide an example in which topographic conditions override the influence of climate.

TABLE V.—CHARACTERISTIC CLAY MINERALS OF DIFFERENT SOIL TYPES.

Climate.	Soil.	Characteristic clay mineral group.
Arctic.	Tundra.	Mica type.
Cold moist temperate.	Podzol.	Kaolinite type.
Moist temperate.	Degraded chernozem.	Kaolinite type.
Semi-arid.	Chernozem.	Montmorillonite type.
Arid.	Chestnut soils.	Montmorillonite type.
Hot, alternate wet and dry seasons.	Red earths.	Kaolinite type.
Hot, alternate wet and dry seasons.	Black earths (regur).	Montmorillonite type.
Moist tropical.	Laterite.	Kaolinite type.

A factor of very great importance, mostly as yet unknown, is the distribution of "trace" elements in soils, in relation to the original rock materials and the special processes of weathering and zoning involved. As many trace elements, such as boron, fluorine, selenium, cobalt, copper, molybdenum, manganese, etc., are of great importance in the production of crops and live stock (Watson, *Chem. and Ind.* 1944, 138; Mitchell, *Proc. Nutrition Soc.* 1944, Vol. I, No. 3), it will be necessary to study the geochemistry of trace elements throughout the processes of weathering and in the assemblages of soil minerals. An observation of general importance is the considerable concentration of many "trace" elements in the inorganic material of the humus layer of forest soils, which seems to be reflected in the concentration of trace elements in the ash of certain fossil coals (Goldschmidt, *Ind. Eng. Chem.* 1935, 27, 1100; Gibson and Selvig, *U.S. Bur. Min., Tech. Paper* 669, 1944).

The fate of fertiliser elements, such as potassium, phosphorus, nitrogen, and calcium, in soils and in soil minerals, has been the subject of many investigations. The fixation and availability of potassium in soils is related to

phenomena of ion adsorption or ion exchange, phenomena which have been found to be closely related to ionic sizes and ionic potentials, a most important factor being the similarity of radii between univalent potassium and hydroxonium ( $H_3O^+$ ) in such minerals as hydromica. The fixation of phosphorus in soils seems to be closely related to the contents of free hydroxides of trivalent elements (iron and aluminium), which tend to form insoluble complexes with phosphoric acid in acid soils. In less acid or alkaline soils, the addition of phosphate may give rise to the formation of insoluble phosphates, fluorophosphates (Nagelschmidt and Nixon, *Nature*, 1944, 154, 428), and hydroxyphosphates of calcium. In the first process the degree of oxidation of the iron ions seems to be very important, ferric iron causing fixation, and reduction to ferrous iron causing release of phosphoric acid, as in corresponding processes in fresh water ecology (Einsele, *Archiv Hydrobiologie*, 1938, 33, 361; cf. Glentworth, *Trans. Roy. Soc. Edin.* 1944, 61, 149). In the second process the presence of available fluorine may prove to be a factor.

The geochemistry of nitrogen in soils is without doubt influenced by the close similarity in ionic radii of the univalent cations of ammonium and potassium in the processes of base exchange. Important problems are related to the activity of molybdenum and possibly vanadium in the fixation of atmospheric nitrogen by nitrogen-fixing bacteria. According to other geochemical experience, the vanadium is probably concentrated in minerals of hydrated ferric iron, and the molybdenum possibly in the soil minerals of trivalent or quadrivalent manganese. The mobility and migration of manganese and molybdenum are dependent to a great extent upon their stage of reduction or oxidation.

Reduction and oxidation potentials generally are of very great importance in the geochemistry of minerals under various conditions. It is clearly understood that the electrochemical potential of reduction to the metallic state is the factor that decides which elements can be expected to occur in the metallic state in terrestrial materials. Mineralogical experience shows that a reduction potential of about  $-0.13$  v. (lead) is the limit for the occurrence of free metals as terrestrial minerals formed from aqueous solutions. It is possible that the similarity in the reduction potentials of the three elements silver, gold, and tellurium is a reason for their frequent very close association in hydrothermal ore deposits. In the mineral assemblages formed from anhydrous melts, as in meteorites, the usual limit is given by the reduction potential of iron.

Reduction-oxidation conditions not only influence the occurrence of uncombined metallic elements, but are also of the utmost importance for the geochemistry of elements existing in more than one stage of ionisation. This will be clearly understood by a consideration of some examples. Bivalent iron has a radius (0.82 Å.) close to that of magnesium (0.78 Å.), while the radius of trivalent iron (0.67 Å.) like that of trivalent vanadium (0.65 Å.) and trivalent chromium (0.64 Å.) is very close to that of trivalent aluminium (0.57 Å.). Therefore the geo-

chemistry of these elements in the tervalent state, especially in the sedimentary and soil cycles, is characterised by the insolubility of their hydroxides and by their association with aluminium compounds. However, quinquivalent vanadium ( $r$  about 0.4 Å.) and hexavalent chromium ( $r$  about 0.3–0.4 Å.) have such a high ionic potential that they form rather soluble complex oxy-acid anions. Therefore, in a sufficiently oxidising environment, vanadates are formed which are isomorphous with phosphates; and also chromates which, like the vanadates, are much more mobile in nature than the oxygen or hydroxyl compounds of the tervalent chromium ion. Hexavalent molybdenum (in molybdates) is much more mobile than quadrivalent molybdenum.

The highest oxidation-potential in terrestrial mineral associations (nitrates, dichromates, perchlorates, and iodates) is encountered in the nitrate soils and nitrate sediments of the nitre deposits of Chile; high oxidation-potentials are also encountered near the surface of certain ore deposits in hot climates, giving rise, for instance, to vanadates, molybdates, and chromates.

These differences in the geochemical behaviour of polyvalent elements are without doubt of great importance for geochemical processes in soils. Processes of reduction and of oxidation often seem to be associated with bacterial activity. As an example of such a geochemical process of reduction, the formation of hydrogen sulphide, iron sulphide, and free sulphur by reduction of aqueous sulphate solutions by sulphur bacteria may be mentioned; and as an example of the oxidation process, the precipitation of ferric hydroxide by oxidation of the iron ions in ferrous bicarbonate solutions, the increase in ionic potential from ferrous to ferric ions causing the precipitation of ferric hydroxide. Very noticeable, through the formation of multi-coloured mineral associations, are the processes of oxidation and reduction connected with the weathering of ore deposits, especially of sulphide ores. In the "oxidation zone," above the level of ground water, ferric hydroxide or hematite is formed, as well as salts of copper, lead, and zinc with oxy-acids, e.g., malachite, diopside, cerussite, anglesite, pyromorphite, vanadinite, wulfenite, and smithsonite. Below the oxidation zone, below the level of ground water, the solutions containing soluble salts of precious metals, e.g., silver, are subject to reduction by sulphides of base metals such as iron and zinc, and in this "cementation zone" the precipitation of metallic silver and copper, and sulphides and thio-salts of silver and univalent copper (e.g.,  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_3\text{SbS}_3$ ,  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_3\text{AsS}_3$ , and many others), is observed. In the cementation zone remarkable concentrations of valuable metals, derived from large volumes of oxidised poorer ores, are found, and this zone was therefore preferably subjected to mining operations in ancient times. Much of the wealth of the Spanish colonies in America, for example, has been derived from the silver ores accumulated in cementation zones.

A number of important minerals and mineral assemblages owe their origin to processes of metamorphism. Under suitable geological con-

ditions, involving considerable alterations of the two well-known physico-chemical factors, temperature and hydrostatic pressure, and a third factor, mechanical strain, important alterations of minerals, mineral assemblages, and rocks can take place; this is known as metamorphism. Most conspicuous as a rule are those alterations which take place when low-temperature and low-pressure assemblages (e.g., of sedimentary rocks) are subjected to elevated temperatures and pressures by heat from neighbouring masses of magma (contact metamorphism), or strain and heat derived from geotectonic movements such as mountain folding (regional metamorphism or dynamo metamorphism), or the combined effect of these two processes.

By contact metamorphism of hydrolysate sediments, anhydrous aluminium minerals, such as *andalusite* (v. Vol. I, 370b), *cordierite* (v. Vol. VII, 17d), *corundum* (v. Vol. III, 398b), and *spinel* (v. Vol. I, 264c, 284c), may be formed, and carbonate sediments may give rise to various silicates of calcium and magnesium. In many cases the mineral assemblages of contact metamorphism furnish fine examples of equilibrium assemblages in accordance with the phase rule.

In regional metamorphism the conditions of mineral formation are somewhat more complicated since, besides variation of temperature, variation of pressure is a factor of very great importance, giving a large variety of compounds containing water or hydroxyl in the products. As an example, hydrolysates transformed into different types of shales, phyllites, mica schists, and aluminous gneisses may be mentioned. A remarkable feature of high-pressure assemblages is the prevalence of very dense minerals such as *kyanite* (v. Vol. VII, 155c) and *pyrope* (v. Vol. V, 429b and c).

In very many cases metamorphism leaves unchanged the bulk chemical composition of mineral assemblages and rocks (with the exception of volatile constituents such as water and carbon dioxide), affecting only the distribution of constituents between the different individual minerals. There are also, however, many cases in which substantial chemical additions and losses take place, both in contact metamorphism and regional metamorphism, such as the transformation of limestone into lime-iron silicates or of dolomites into magnesite. Such a process, involving chemical transformation of one or more minerals by reactions with solutions or gases, is called *metasomatism*, a process very important for the formation of many useful ores and other mineral materials outside the scope of contact or regional metamorphism. Many important deposits of zinc and lead ores have been formed by metasomatic transformation of limestone and dolomite.

Metasomatic processes of very great geochemical importance are involved in "felspathisation" or "granitisation" in areas of combined contact and regional metamorphism, processes whereby the hydrolysate sediments such as shales can be transformed into gneisses and granite-like rocks (Goldschmidt, *Videnskapselskapets Skrifter*, I, Mat. Naturv. Klasse, Kristiania, 1920, No. 10).

The physico-chemical laws of mass-action can

be applied to the processes of metasomatism, requiring a certain minimum concentration of the invading solutions to effectuate mineral transformation.

The geochemistry of minerals is thus controlled by the atomic or ionic properties of the elements involved, and also by geological environmental factors such as temperature, pressure, and strain, and their changes, reduction-oxidation potentials, diffusion of solutions and gases, and biochemical processes.

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V. M. G.  
A. M.

**MINERVITE.** A hydrated phosphate of aluminium with potassium, of variable composition, derived from organic remains and from cave-deposits of bat-guano. It occurs as white, earthy or pulverulent masses, typical analyses including  $P_2O_5$  39,  $Al_2O_3$  20,  $K_2O$  7,  $H_2O$  29%, and a small quantity of ammonia. The mineral serves as a valuable fertiliser, though produced only on a small scale.

D. W.

**MINETTE.** A French miners' term of local origin now applied both to an igneous rock and to an iron-ore. The name is used in petrology for a dark, fine-grained member of the lamprophyre group, consisting essentially of orthoclase and biotite, and usually occurring in the form of igneous dykes. It sometimes serves locally as a road-metal.

In central Europe the "minette" or oolitic limonite ores of Lorraine and Luxembourg provide the bulk of the raw material for the

French and German steel industries. These ores probably rank second only in importance to the hematites of the Lake Superior region. They are sedimentary deposits, interstratified with shales, limestones, and sandstones of Jurassic age, the ore being composed of soft, earthy, oolitic limonite and subsidiary hematite, with some siderite and the iron silicate, chamosite. The grade of ore is low, averaging Fe 30,  $P_2O_5$  2, CaO 5-12,  $SiO_2$  7-20%. About 50 million tons of "minette" ore are produced annually, and the reserves are estimated at 5,000 million tons.

D. W.

**MINIOLUTEIC ACID** (v. Vol. V, 52d).

**MINIUM.** An oxide of lead,  $Pb_3O_4$ , found only in massive, earthy, or powdery form, and in microscopic crystalline scales of unknown symmetry. Its colour is scarlet or orange-red, and the streak orange-yellow.  $\rho$  4.6, hardness 2½. The mineral becomes black on heating, but the original colour is restored on cooling. It is soluble in hydrochloric acid with evolution of chlorine. Minium is a comparatively rare secondary mineral derived by the alteration of galena and cerussite, and is occasionally found as a coating on ancient leaden objects.

The artificial red lead used as a pigment has the same composition as minium. It may be prepared by heating lead monoxide in air at dull red heat; minute crystals can be grown by heating lead monoxide or carbonate in hot concentrated potassium hydroxide solution.

D. W.

**MINOFER** (v. Vol. I, 446a).

**MINYAK NYATOH** (v. Vol. II, 32c).

**MIOTINE** (v. Vol. II, 200d).

**MIRABILITE**, Glauber's salt. A hydrous sodium sulphate,  $Na_2SO_4 \cdot 10H_2O$ , crystallising in the monoclinic system, sometimes in long needle-like forms, but usually found as efflorescent crusts. It is identical with the artificially produced Glauber's salt or *sal mirabile* of Glauber. Possesses a perfect front pinacoidal cleavage, is white in colour, and is readily soluble in water with a cool and then feebly saline and bitter taste.  $\rho$  1.48, hardness 1½-2. Mirabilite loses its water rapidly in dry air and crumbles to powder. It is deposited from saline waters in arid regions, especially during the winter months, and is extracted from the concentrated brines of bitter lakes. Extensive harvestable deposits occur along the shores of the Great Salt Lake and the Gulf of Karabugaz (Caspian Sea). The mineral is often associated with halite and gypsum, and may occur in lake-bottom deposits interstratified with epsom salts and sodium carbonate.

The annual world production of natural sodium sulphate exceeds 50,000 tons, but the natural compound is now largely displaced by salt cake ( $Na_2SO_4$ ) manufactured from salt. Artificial Glauber's salt is made from salt cake. The anhydrous sulphate is used extensively in the manufacture of wood pulp for Kraft paper, and in making rayon, textiles, heavy chemicals, glass, dyes, soap, paint, etc. The hydrous salt is employed in dyeing and as a medicine, especially for cattle. Mirabilite is dehydrated for shipment as "crude salt cake," which can be

dissolved in water and recrystallised in the form of Glauber's salt.

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D. W.

**MIRBANE, ESSENCE OF, *Myrbane*,**\* *essence of*, old names for nitrobenzene (Vol. I, 676b).

J. N. G.

**MISCHMETALL** (v. Vol. II, 516b).  
**MISCIBILITY OF LIQUIDS** (v. PHASE RULE).

**MISO** (v. Vol. V, 59c).

**MISPICKEL** (usually known as Arsenopyrite, or Arsenical Pyrites). A mineral consisting essentially of iron arsenide-sulphide,  $\text{FeAsS}$ , but with cobalt usually replacing a part of the iron. High-cobalt varieties are known as *glaucofol*. It has been shown recently that arsenopyrite is not orthorhombic, as formerly considered, but monoclinic, or perhaps triclinic. Crystals prismatic, either long or short, the prism zone being often striated vertically and the domes grooved horizontally; twinning produces pseudo-orthorhombic forms, star-shaped trillings, and repeated twins, as in marcasite. The mineral commonly occurs in granular or massive form, and when not tarnished it has a silver-white colour inclining to steel-grey, with a dark greyish-black streak. It is liable to tarnish to a pale copper-colour on exposure, and has a bright metallic lustre. Under the ore-microscope, in polarised light, the mineral exhibits strong anisotropism. When heated on charcoal or struck with steel it emits a characteristic garlic odour.  $\rho$  5.9–6.2, hardness  $5\frac{1}{2}$ –6.

Arsenopyrite is the most important source of arsenic. It is frequently found in tin and tungsten ores, and in many gold, silver, copper, lead, and zinc deposits, the most notable being that of Boliden in Sweden, which is alone capable of supplying enough arsenic for the whole world. About 50,000 tons of "white arsenic" are normally produced annually as a by-product of smelter smoke from arsenical ores containing arsenopyrite and other less common arsenic minerals, such as enargite. Sweden, France, U.S.A., and Mexico are the chief producers of arsenic.

Arsenic is principally used in the form of white arsenic, or arsenious oxide,  $\text{As}_2\text{O}_3$ , which is widely employed as a weed killer and for the manufacture of insecticides and wood and leather preservatives, glass, dyes, and pigments. Metallic arsenic is alloyed with lead in shot metal.

D. W.

**MISTS, PARTICLE SIZE IN** (v. Vol. IV, 95b).

"**MITIGAL**" (v. Vol. VII, 593d).

**MITIS GREEN.** *Schweinfurt Green* (Vol. I, 478a).

J. N. G.

\* The origin of Mirbane is obscure; the derivation is not given in the leading dictionaries in the British Museum.

**MITRAGYNE AND ALKALOIDS OF MITRAGYNA SPECIES.** The botanical problem of the *Mitragyna* species (Fam. *Rubiaceæ*, sub-group *Cinchonoideæ*) is complicated, and it seems doubtful whether all bases are traced from the correct source. According to Raymond-Hamet and Millat (cf. Bull. Sci. Pharmacol. 1933, 40; 593, with interesting botanical details), four Asiatic and two African *Mitragyna* species are known:

1. *M. parvifolia* Korthals.
2. *M. rotundifolia* O. Kuntze (syn. *M. diversifolia* Havil.).
3. *M. speciosa* Korthals.
4. *M. tubulosa* O. Kuntze.
5. *M. inermis* O. Kuntze (syn. *M. africana* Korthals).
6. *M. stipulosa* O. Kuntze (syn. *M. macrophylla* Hiern).

Under the name of "Kratom" the leaves of *M. speciosa* are chewed as a narcotic in Siam by habitués, who, like the Coca addicts in S. America, are stated to be able to endure great fatigue in great heat (T. A. Henry, "Plant Alkaloids," 3rd ed., Churchill, 1939, p. 623). The bark of *M. africana* is used in Senegal as febrifuge. For the pharmacology of mitragynine, cf. Grewal (J. Pharm. Exp. Ther. 1932, 46, 251), and for mitrinermine, cf. Perrot, Raymond-Hamet, and Millat (Bull. Sci. Pharmacol. 1936, 43, 694). None of the mitragyna bases is of any practical use for medical purposes.

Mitragynine,  $\text{C}_{22}\text{H}_{30}\text{O}_4\text{N}_2$  (or possibly  $\text{C}_{22}\text{H}_{32}\text{O}_4\text{N}_2$ ), was first isolated by Field from *M. speciosa* (J.C.S. 1921, 119, 887). It was re-extracted (yield 0.2%) and re-investigated by Ing and Reason (*ibid.* 1939, 986). Mitragynine is an amorphous, colourless solid; it distils unchanged at 230–240°/5 mm.; m.p. after distillation, 102–106°; it is a monoacidic base (like all mitragyna alkaloids), yielding an amorphous *monomethiodide*, m.p. 211.5°. The *picrate* forming orange-red slender needles from methanol, m.p. 223–224°, is the only salt suitable for the initial purification of the alkaloid; *hydrochloride*, rhomb-shaped leaflets, m.p. 243°; *hydrogen fumarate* cream-coloured felted mass of needles from methyl ethyl ketone, decomp. between 190° and 200°; *cinnamate*, m.p. 155°. Mitragynine contains three methoxyl groups; by the action of alkali and methanol it is converted into an amphoteric monocarboxylic acid,  $\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2$ , m.p. 280°, and a basic substance,  $\text{C}_{23}\text{H}_{34}\text{O}_6\text{N}_2$ , regenerating the original base with alcoholic hydrogen chloride and yielding the amphoteric acid on further treatment with alkali. By simply methylating this amphoteric acid, mitragynine is not regenerated. Dehydrogenation with selenium and zinc-dust distillation yielded no definite results. Besides mitragynine, a second amorphous base, with an amorphous *picrate*, was obtained from the same plant (yield 0.27%).

Mittraversine,  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2$ , isolated from *M. diversifolia* (Field, *l.c.*), crystallises from methanol, m.p. 237°. The *hydrochloride* forms rhomb-shaped leaflets, m.p. 208–210°. Mittraversine contains two methoxyl groups. Raymond-Hamet and Millat (J. Pharm. Chim. 1937,



[viii], 25, 391) have isolated from the same plant an alkaloid with m.p. 263.5–264.5°, with about the same molecular formula as Field's compound.

Rotundifoline,  $C_{22}H_{26}O_5N_2$ ,  $[\alpha]_D^{15} +12.4^\circ$  ( $c=2.14$ , in chloroform), isolated from *M. rotundifolia*, yield about 0.005% (Barger, Dyer, and Sargent, J. Org. Chem. 1939, 4, 418), crystallises in slender glistening prisms from methanol, m.p. 233–234°, soluble easily in chloroform, moderately in acetone, ethyl alcohol, and benzene, and sparingly in ether.

Mitraspecine,  $C_{25}H_{36}O_5N_2$ , was isolated by Denis (Amer. Chem. Abstr. 1939, 33, 1741) from *M. speciosa*; it forms monoclinic platelets from ethyl alcohol, m.p. 244–245°,  $[\alpha]_D^{25} -59.15^\circ$  (in chloroform), soluble in ethyl alcohol, benzene, and acetone, but almost insoluble in ether. The picrate has m.p. 136°. Mitraspecine contains three methoxyl groups. The bark of *M. speciosa* yields 5% of the alkaloid, in contrast to the 0.2% content of the wood.

Mitrinermine,  $C_{22}H_{28}O_4N_2$ ,  $[\alpha]_D^{12} -24^\circ$ , was first isolated by Raymond-Hamet and Millat from *M. inermis* (Compt. rend. 1934, 199, 587) and from *M. stipulosa* (J. Pharm. Chim. 1934, [viii], 20, 577). It crystallises in fine needles from acetone, m.p. 215–216°, and is very soluble in the usual solvents; it contains two methoxyl groups. Raymond-Hamet (Bull. Sci. Pharmacol. 1940, 47, 194) has identified the alkaloid crossoptine (from *Crossopteryx* spp.) with mitrinermine. Barger, Dyer, and Sargent (l.c.) have isolated mitrinermine from *M. rotundifolia* (yield 0.03%) and examined its absorption spectrum; they have also found that it is identical with *rhynchophylline*, which Kondo (Amer. Chem. Abstr. 1928, 22, 3166) isolated from *Ourouparia rhynchophylla*. Similarly to mitragryne, mitrinermine yields by alkaline hydrolysis an amphoteric acid which, when methylated, does not regenerate the original base.

Mitraphylline,  $C_{21}H_{26}O_4N_2$ ,  $[\alpha]_D^{25} -7.7^\circ$  (in chloroform) was isolated by Michiels from what was believed to be *M. macrophylla* Liern. (Amer. Chem. Abstr. 1926, 20, 964; 1932, 26, 3070), but was later found to be *Adina rubrostipulata* (ibid. 1936, 30, 7780); it is therefore closely related to the mitragyna alkaloids (cf. Denis, *ibid.* 1928, 22, 301). It crystallises in fine needles from acetone, m.p. 262–263°.

Authentic *M. macrophylla* was extracted by Larrieu (Pharm. Thesis, University of Paris, 1930). Raymond-Hamet and Millat have demonstrated (Amer. Chem. Abstr. 1935, 29, 4133) that the alkaloid of this plant is mitrinermine; they have also reinvestigated Michiels' specimen of mitraphylline (ibid. 1936, 30, 1379) and are of the opinion that it is the mono-methoxy derivative of mitrinermine. An unnamed alkaloid is also known to be present in *M. parvifolia* Korth., but details are not given (Hooper, Pharm. J. 1907, 78, 453).

Little is known about the constitution of the mitragyna bases; no doubt they are indole-alkaloids carrying one or several methoxyl groups but no NMe-groups, and they are methyl esters of unknown amphoteric acids.

Schl.

MITSCHERLICH PULPS (r. Vol. II, 461c).

MITTLER'S GREEN is Guignet's Green (Vol. III, 107b; IV, 279c) or a mixture containing this pigment and barium sulphate.

J. N. G.

MIXED CRYSTALS (r. PHASE RULE).

MIXTURES, AZEOTROPIC (r. Vol. IV, 51b).

MKANYI FAT (MSAMBO FAT) is the hard white fat (m.p. 40–46°) obtained from the seeds of the East African tallow tree (*Allanblackia stuhlmannii* Engl. (syn. *Stearodendron stuhlmannii*) (Palm. Guttiferae). It is used locally by the natives for edible purposes, and would be suitable for the manufacture of soap or stearine. The fatty acids consists of (approximately) palmitic acid 3, stearic acid 53, and oleic acid 44%. The fat itself consists chiefly of oleo-distearin (63–65%, probably entirely the  $\beta$ -oleo- $\alpha'$ -distearin) and di-oleostearins, with a very little (probably not over 1.5%) of palmito-stearins (cf. Heise, Arb. Kaiserl. Gesundheitssamt, 1896, 12, 540; Krause and Diesselhorst, Tropenpfl. 1909, 13, 286; Anon., Bull. Imp. Inst. 1929, 27, 455; Hilditch and Salatore, J.S.C.I. 1931, 50, 468r; 1933, 52, 101r).

Similar fats are obtainable from "Kisidwe" seeds derived from *A. floribunda* Oliv. ("Bouandja fat"), from the seeds of *A. floribunda* var. *Kisonghi*, Verm. (Pieraerts and Adriaens, Les Mat. grasses, 1929, 21, 8510, 8539; Anon., Bull. Imp. Inst. 1929, 27, 455; Meara and Zaky, J.S.C.I. 1940, 59, 25), from *A. parviflora* (Meara and Zaky, l.c.), and from the seeds of *A. klainri* Pierre (Adriaens, Les Mat. Grasses, 1933, 25, 9931, 9961).

E. L.

M.N.T. (r. Vol. IV, 466b).

MOCHA-STONE (r. Vol. I, 164a).

MOCHYL ALCOHOL (r. Vol. I, 602d).

MODDITE (r. Vol. IV, 519b).

MOEBIUS PROCESS (r. Vol. VI, 108a).

MOHAIR (r. Vol. IV, 124c).

MOHAWKITE (r. Vol. IV, 55c).

MOHRI (r. Vol. I, 123a).

MOHUA BUTTER (r. Vol. I, 653a).

MOIRÉ MÉTALLIQUE. Tin-plate (r. Vol. VII, 52c), tinned sheet iron, acquires a variegated crystalline appearance by a heat treatment followed by etching with acids. The sheet is heated at about 230°C. until the surface just begins to flow, cooled in water, and then dipped momentarily into diluted *aqua regia* (e.g.,  $HCl:HNO_3:H_2O=1:3:40$ ). In Habernicht's U.S.P. 300599, the sheet is quickly washed in 4% sodium hydroxide solution before etching. Finally it is washed in water, dried, and lacquered.

J. N. G.

MOISSANITE. Naturally occurring silicon carbide, SiC, crystallised in the rhombohedral system, and identical with the artificial product known as carborundum. As minute, green, hexagonal plates, associated with microscopic diamonds, it was detected by Henri Moissan (1852–1907) in the meteoric iron of Cañon Diablo in Arizona.

L. J. S.

**MOLAR FRACTION (or MOL FRAC-TION).**

**Definition.**—If a system contains more than one kind of molecular species, the proportion of any particular constituent in the mixture can be expressed by the molar fraction, which is simply the ratio of the number of molecules (or g.-mol.) of that constituent to the total number.

Thus, if the mixture contains  $n_A$  molecules (or g.-mol.) of A,  $n_B$  molecules of B,  $n_O$  molecules of C, etc. . . ., then the molar fraction of A ( $N_A$ ) in the mixture is:

$$N_A = \frac{n_A}{n_A + n_B + n_O + \dots}$$

A similar expression gives the molar fraction of B, C, etc., and, of course, the sum of all the molar fractions is unity.

$$N_A + N_B + N_O + \dots = 1.$$

Molar fraction is often the most convenient unit for expressing the composition of a mixture, and is clearly the most fundamental. It is commonly used in the theory of the "osmotic" (or "colligative") properties of solutions; for example, in dilute solutions the lowering of partial vapour pressure, the osmotic pressure, the elevation of boiling-point, and the depression of freezing-point are all approximately directly proportional to the molar fraction of solute (or, if more than one solute is present, to the sum of the molar fractions of all the solutes). Molar fraction is employed very extensively in the modern thermodynamic theory of solutions (see, for example, E. A. Guggenheim, "Modern Thermodynamics," London, 1933).

Molar fraction is, of course, related in a simple manner to the practical units of concentration, since the mass ( $m_A$ ) of  $n_A$  molecules of molecular weight  $M_A$  is given by

$$m_A = n_A M_A / N,$$

where  $N$  is Avogadro's Number (the number of molecules in 1 g.-mol., i.e.,  $6.06 \times 10^{23}$ ). Hence, if the composition of a mixture is known in mass units, the molar fractions can be obtained from expressions such as:

$$N_A = \frac{m_A / M_A}{m_A / M_A + m_B / M_B + m_C / M_C + \dots}$$

Similarly, by means of the gas laws the molar fraction of a constituent of a gaseous mixture can be calculated from a knowledge of the partial pressures of the various components.

J. A. K.

**MOLECULAR BEAMS** (or molecular rays) are streams of molecules moving through a high vacuum in a narrow bundle, with thermal velocities. A molecular beam is produced by letting molecules escape through a small orifice into an evacuated container, and placing a screen with a small opening across their path so that only a narrow bundle of molecules can pass through. The first experiments with molecular rays (by L. Dunoyer, *Le Radium*, 1911, 8, 142) were undertaken to provide direct evidence for the kinetic theory of gases. Later the method was improved and used by O. Stern and his school to study the deflection of atoms and molecules in magnetic fields, and for other problems.

In only a few other laboratories has work on molecular rays been taken up; prominent among them is that of I. I. Rabi and collaborators. The method of molecular beams and earlier results are described by R. G. J. Fraser, "Molecular Rays," Cambridge University Press, 1931.

**Production.**—The method of producing molecular beams depends on the character of the substance in question. Substances which have too low a vapour pressure at room temperature (e.g., metals, salts, etc.) must be heated in an "oven," a closed container with a narrow opening (generally a slit) through which the vapour molecules can escape. The oven is placed inside a larger container in which a high vacuum is maintained. A second slit, the "collimator," is placed some distance from the oven in order to allow the passage of a narrow bundle of molecules only. The other molecules are condensed on the collimator or the walls of the apparatus, or on special condensing surfaces cooled, e.g., with liquid air. The collimation is often achieved in two steps, first by a "fore-slit" which is placed at about 1 cm. from the oven slit, and then by the collimator proper at a greater distance. The foreslit forms the only opening in a partition wall which divides the apparatus in two compartments, which are exhausted by separate pumps. This is done because the oven generally gives off some gaseous products, and the beam would suffer considerable scattering if it were to run in this gas for its whole length. With the arrangement described, the beam passes into a higher vacuum on going through the fore-slit.

Gases (or generally substances with a sufficient vapour pressure at room temperature) need no heating, yet the opening through which they are allowed to escape into the vacuum is generally called the oven slit. The use of a fore-slit and a powerful pump for removing those molecules which do not form part of the beam is essential. For special purposes the oven slit may be cooled or heated, in order to get a higher or lower average velocity of the molecules. Beams of atomic hydrogen or oxygen have been produced by passing the gas through an electric discharge tube immediately before it arrives at the oven slit.

As the pressure of the gas or vapour in the oven is increased the beam intensity at first rises proportionally with the pressure. If, however, the pressure is raised beyond the point where the mean free path is equal to the width of the slit, collisions between the molecules in front of the oven slit become frequent and the beam gets broadened. (This phenomenon is also described by saying that the escaping gas forms a cloud in front of the oven slit.) In addition, the intensity loss due to scattering of the beam in the gas between oven slit and fore-slit increases with increasing pressure, with the result that the beam intensity passes through a maximum. The best conditions for producing intense molecular beams have been laid down by O. Stern (*Z. Physik*, 1926, 39, 751).

**Detection.**—For the detection of molecular beams, several methods have been developed. In the case of solids a receiving plate (of polished metal or glass) may be placed across the beam.



A visible deposit is formed by the condensing molecules; the intensity of the beam may be estimated—rather inaccurately—from the time (a few seconds to several hours) which elapses before the deposit becomes visible. If the beam is very weak, the yet invisible trace can be “developed” by admitting, for instance, mercury vapour (cigar smoke, too, has been tried with some success). Alternatively, the collector can be sensitised by depositing a thin layer of metal before exposing it to the beam. The collector must, in general, be cooled, for instance by liquid air, since molecules arriving one by one at a surface of a different material tend to evaporate again unless they meet another similar atom with which they can form the rudiment of a crystal lattice. At temperatures such that this re-evaporation is appreciable, the time required to form a visible trace increases rapidly with decreasing beam-intensity. Single atoms also tend to migrate along the surface, and very fine traces thereby become both blurred and weakened. For these various reasons the condensation of the beam on a collecting plate has now been practically abandoned as a method of detection, but the study of this phenomenon offers interesting information regarding the interaction of the beam molecules with the receiving surface.

A visible trace can be obtained from beams of atomic hydrogen, by letting them impinge upon a surface of molybdenum trioxide, which thereby becomes reduced and blackened. Similarly, a target of litharge can be used for atomic oxygen.

Beams of gas molecules or atoms can be measured quantitatively by observing the increase in pressure inside a closed container into which they are allowed to enter through a small opening. The pressure in this container rises until the number of molecules escaping through the opening (the receiving slit) equals the number brought in by the beam. The equilibrium pressure is thus proportional to the beam intensity. By moving the receiving slit across the beam its intensity distribution can be quantitatively explored. A very sensitive manometer has to be used in measuring the pressure rise, which is of the order of  $10^{-5}$  mm. of mercury, or less. O. Stern developed an improved Pirani (hot-wire) manometer which allowed him to detect pressure changes of a few  $10^{-9}$  mm. To eliminate pressure fluctuations in the vacuum (which are often many times greater than the pressure built up by the beam) he used two similar manometers connected to similar slits, one of which was placed away from the beam; the two manometers formed part of a Wheatstone bridge in such a way that an equal pressure change on both manometers gave no galvanometer deflection. The receiving slit is often made fairly deep (like a slit cut with a thin saw in a thick board) so as to delay the escape of molecules without impeding the entry of the beam. This increases the equilibrium pressure, but also the time required to establish equilibrium, and it is therefore important to keep the volume of the manometer as small as possible. Manometers of less than 1 ml. have been made (O. R. Frisch and O. Stern, *ibid.* 1933, 85, 4; J. M. B. Kollogg, I. I. Rabi, N. F. Ram-

sey, and J. R. Zacharias, *Physical Rev.* 1939, [ii], 56, 728). A special type of ionisation manometer has also been tried (I. Estermann and O. Stern, *Z. Physik*, 1933, 85, 135).

A very elegant and sensitive method of detection, first employed by J. B. Taylor (*ibid.* 1929, 57, 242) depends on the fact that certain molecules, in particular those containing alkali elements, become ionised if they impinge on hot tungsten. A tungsten wire is placed in the path of the beam, and a negative electrode near or around the wire serves to collect the ions given off. The current is proportional to the number of molecules which hit the wire per unit time, and an electrometer or sensitive galvanometer permits the detection of very weak beams. The sensitivity may be further increased by letting the beam condense on the cold wire for some time and then observing the ballistic deflection caused by the sudden release of the accumulated amount on heating the wire. Certain molecules which are not ionised by pure tungsten may be detected if the wire is previously covered with a layer of oxygen, whereby its work function is raised.

**Application.**—The technique of molecular beams has been applied to a great variety of problems. In the first instance they were used to verify in the most direct manner the behaviour of molecules as predicted by the kinetic theory of gases. On increasing the pressure in the container through which the beam passes, the beam intensity was found to decrease exponentially. From the rate of decrease, the mean free path of the molecules could be calculated. The value found was considerably smaller than the value calculated, e.g., from viscosity data. The reason is that a very small angular deflection is sufficient to remove a molecule from the beam, whereas viscosity phenomena are connected with large-angle deflections, for which the colliding molecules must approach more closely. The correctness of this interpretation is borne out by the fact that very narrow beams have a shorter mean free path than broader ones. Attempts have also been made to observe directly the angular distribution of molecules scattered from the beam by collisions with gas molecules (of the same or a different kind), and direct evidence was obtained for the strong prevalence of forward scattering, which had been deduced, e.g., from the temperature dependence of viscosity (F. Knauer, *ibid.* 1932, 80, 80).

The Maxwell distribution of molecular velocities was another prediction of the kinetic theory which could be tested directly by molecular beams. Stern rotated the whole evacuated container, and showed that the deposit formed by the beam on the collecting plate is shifted and blurred to an extent corresponding to the amount by which the collector moves during the passage of the molecules from the collimator to the collector. It is also possible to select molecules within a narrow velocity interval, by passing the beam through a system of two rapidly rotating slotted wheels (somewhat like that in Foucault's measurement of the velocity of light). By varying the speed of the wheel and observing what fraction of the beam is passed, the velocity distribution can be deter-

mined with considerable accuracy, and is found to be in complete agreement with Maxwell's prediction.

Experiments on the reflection of molecular beams from solid surfaces have revealed some very interesting phenomena connected with the wave properties of streams of moving particles. On the whole, the assumption of the kinetic gas theory that molecules are reflected according to a cosine law (like light from a dull white surface) has been found correct. The reason is that even on the most highly polished surface there are irregularities much larger than the de Broglie wave-lengths of molecules moving with Maxwellian velocities. The effect of these irregularities is reduced at glancing incidence (when, for instance, a ground-glass disc shows some specular reflection of light) and for light molecules (helium, hydrogen), for which the wave-length is largest. Very slight specular reflection was indeed observed from polished metal at a glancing angle of a few minutes.

From a cleavage surface of a lithium fluoride crystal (and to a lesser extent, from other alkali halides), however, an appreciable part of a beam of hydrogen or helium is reflected in mirror-like fashion. In addition, diffracted beams are observed, the direction of which agrees accurately with that calculated from the properties of the cross-grating formed by the top layer of atoms in the crystal lattice. By studying the diffraction of beams of helium from which all molecules except those within a narrow velocity interval had been removed by rotating tooth-wheels (*see above*) the de Broglie relation  $\lambda = h/mv$  between momentum,  $mv$ , and wave-length  $\lambda$  (where  $h$  = Planck's quantum of action) was verified with great accuracy (I. Estermann, O. R. Frisch, and O. Stern, *ibid.* 1932, 73, 348).

The quantitative study of these reflection and diffraction phenomena would no doubt enable fairly detailed conclusions to be drawn about the forces acting between the beam molecules on one hand and the crystal surface on the other. One result in this direction is the interpretation of certain irregularities observed in the reflection and diffraction of beams of helium atoms on a surface of lithium fluoride. It had been observed that the intensity of the reflected beam varies in a very marked fashion if the crystal is rotated in its own plane, and similar variations occur in the diffracted beam. It was suspected that these irregularities occurred whenever one of the diffracted beams fell into the plane of the crystal, but the directions in which irregularities were actually found did not agree with this idea. J. E. Lennard-Jones and A. F. Devonshire (*Nature*, 1936, 137, 1069) showed that quantitative agreement could be obtained if due attention was paid to the attraction between the surface of the crystal and the beam molecules, and concluded that there are at least two energy states for the helium atoms adsorbed on the cncbe face of lithium fluoride, the heats of adsorption being 57.5 and 129 g.-cal., respectively.

The reflection of light molecules from crystal surfaces is essentially a wave phenomenon. The "bumpiness" of the crystal surface, due to its atomic structure, merely causes the appearance of diffracted beams, while the reflected

beam (diffraction of zero order) remains completely sharp. (A very slight broadening in certain cases was traced to imperfections of the crystal.) With heavy atoms (zinc, cadmium, mercury) a "classical" type of reflection was observed (A. Ellett and H. F. Olsen, *Physical Rev.* 1931, [ii], 38, 977; R. M. Zabel, *Bull. Amer. Physical Soc.* 1932, 7, 29; B. Josephy, *Z. Physik*, 1933, 80, 755). Here the wave-length is so small that different diffraction orders are not resolved but appear as a broadening of the reflected beam, which can be described in terms of reflection of elastic spheres from a corrugated surface.

Perhaps the most important (certainly the most numerous) applications of molecular beams are those based on their deflection in magnetic fields. It was an early conclusion from quantum theory that the possible orientations of molecules in a magnetic field are quantised, that is, that only a finite number of orientations are possible. In particular, for a system with a momentum of  $h/4\pi$  (such as, for instance, an alkali atom), two positions only exist, viz. those in which the magnetic moment of the system is either parallel or antiparallel to the magnetic field. If a beam of atoms of that kind passes through an inhomogeneous magnetic field in which the field is stronger, say, to the right of the beam and weaker to the left, then those atoms which are orientated parallel to the field are deflected to the right, whereas those with the antiparallel orientation are deflected to the left. Stern and Gerlach were the first to show that a beam of silver atoms is indeed split into two distinct beams (*Ann. Physik*, 1924, [iv], 74, 673). This was direct evidence for the "space quantisation" predicted by quantum theory. According to classical physics, atoms with all kinds of orientations should have been represented in the beam, and their deflection in the inhomogeneous magnetic field should merely have caused the beam to be broadened.

The magnetic field used by Stern and Gerlach was produced by an electromagnet, one pole piece of which had a sharp edge facing a groove in the other pole piece. Thus the field intensity varies rapidly from a high value near the edge to a low value in the groove. The beam is aimed so as to run parallel to the edge and fairly near to it. For accurate measurements it is necessary to know the field gradient accurately, which requires rather laborious measurements. Rabi suggested an alternative arrangement in which the beam is directed, at an angle, against the edge of a homogeneous field formed between flat parallel pole-pieces. On entering the field the beam passes through a region of inhomogeneity and suffers deflection. It is not necessary, however, to measure the field in this region, since the total deflection depends only on the value of the magnetic field where it has become homogeneous, and on the angle between the beam and the edge of the field. (The phenomenon is, indeed, analogous to the refraction of light on passing from one medium to another.) Another way is to use one or more wires through which an electric current is passed; the field thus produced can be calculated, but it is difficult to get very strong fields by this method.

Because of their different velocities, individual beam molecules suffer different deflections, and the two parts into which the beam is split are broadened. By applying the ionisation method to the detection of a beam of alkali atoms it was possible to measure the intensity distribution accurately, and to show that it does indeed agree with the Maxwell distribution, as expected. In the course of such experiments a small undeflected beam was noticed, and ascribed to the (non-magnetic) diatomic molecules. The splitting of the beam in the magnetic field therefore constitutes in some cases a reliable and accurate analysis of the beam into its atomic and molecular components. By varying the temperature and pressure of the oven and oven slit, it was possible to determine the heat of dissociation of the molecules  $K_2$ ,  $Na_2$ , and  $Li_2$  (L. C. Lewis, *Z. Physik*, 1931, 69, 786).

Only one successful attempt has been made so far to determine the magnetic moment of an atomic nucleus by the deflection of a molecular beam, caused by this moment. Molecular hydrogen is probably the only substance suitable for this method, since its molecules carry no electronic moment and the rotation of the molecule (which produces a magnetic moment of similar magnitude to the nuclear moment) can be restricted to its two lowest quantum-states by cooling the oven with liquid air. In view of the smallness of the moment to be measured (about one-thousandth of that of an electron, as carried by an alkali atom) a very long and narrow beam and a very strongly inhomogeneous field had to be employed (O. Stern *et al.*, *ibid.* 1933, 85, 4). The result was unexpected: it was found that the magnetic moments of proton and electron were not—as had been thought—in the inverse ratio of their masses, the moment of the proton being about 2.5 times the expected value.

The problem of measuring nuclear moments was very successfully solved by Rabi and his school, who used several indirect methods. In one of them, the deflection of atoms carrying an electron moment (e.g., hydrogen or alkali atoms) is studied in a deflecting field which is so weak that coupling between the nuclear moment and the electronic moment is only partly destroyed. This is the case if the deflecting field is about as strong as the field caused by the nucleus at the average distance of the electron which produces the electronic moment. The theory of these deflections is practically identical with the theory of the anomalous Zeeman effect (the splitting-up of spectral lines in weak magnetic fields), and the molecular method gives no information which could not, in principle, be obtained from a study of the Zeeman effect. The advantage of the molecular beam method is its much greater resolving power and the fact that it gives directly the splitting of one term (in general the ground term), whereas a spectral line corresponds to the transition between two levels and its Zeeman pattern is therefore more complicated. For an accurate measurement of a nuclear moment the electronic wave-function of the atom in question is required, and this is known accurately for the simplest atoms only.

In the case of the proton and the deuteron,

the results obtained by the deflection of molecules were essentially verified, and approximate magnetic moments were found for some other nuclei. Perhaps the main advantage of Rabi's method is that it allows the angular momentum of the nucleus in question to be found in a reliable way. (The spectroscopic determination of angular momenta is a very delicate problem.) The procedure is based on the fact that for certain values of the magnetic field the contributions of the nucleus and the electron to the magnetic moment of the atom may cancel, so that a certain proportion of the atoms passes undeflected. The receiver is set at the position of the undeflected beam and the magnetic field is varied. At each of the critical field-values a sharp maximum in beam intensity is observed, and the number and position of these maxima yields directly the angular momentum.

The latest and most successful method for measuring nuclear magnetic moments was also developed by Rabi and his school (*Physical Rev.* 1938, [ii], 53, 318; 1939, [ii], 55, 526) and is frequently called the method of radio-frequency spectra. The arrangement is more complicated in so far as the beam passes through three different magnetic fields in succession. The first and third are inhomogeneous fields of the usual type. After being split up in the first field, the beam traverses a slit which allows one component only to pass through. The inhomogeneity in the third field is opposite to that in the first, so that the atoms suffer a deflection in the opposite sense and are focussed on the detector. The second field is a strong homogeneous one, on which is superimposed a weak radio-frequency field. If the quantum energy  $h\nu$  of the radio-frequency happens to be equal to the energy difference between two adjacent orientations of the nucleus, some of the nuclei will take up (or give up) a quantum and assume a new orientation in the magnetic field. In consequence, some of the molecules will be deflected in the wrong direction on passing through the third field, and the intensity observed by the detector will be diminished. The phenomenon can also be described as a resonance between the Larmor frequency of the nucleus in the magnetic field and the radio frequency superimposed on it. In looking for these resonances, the radio frequency is kept constant and the magnetic field is altered in small steps. The recorded beam-intensity as a function of the magnetic field shows a number of exceedingly sharp minima, corresponding partly to the various nuclei represented in the beam, and partly to moments caused by molecular rotations (electronic moments have a much higher Larmor frequency and are not observed). Assignments are made with the help of beams of molecules of different chemical compounds, and by the different amplitude of the minima. The method gives the gyromagnet-ratio, that is the ratio of the magnetic moment to angular momentum. So far this ratio has been measured for more than 20 different kinds of nuclei, and the results are of great interest for nuclear theorists. From certain anomalies in the radio-frequency spectrum of atomic deuterium, Rabi concluded that the deuteron possesses an

appreciable electrical quadrupole moment, a result of fundamental importance for the theoretical study of the forces between nuclear particles.

The deflection of molecular beams in inhomogeneous electric fields has been observed, and several attempts have been made to determine thereby the electric dipole-moment and the polarisability of certain organic molecules which are insoluble in non-polar solvents. Only qualitative results were obtained (*see* Fraser, *op. cit.*, and M. Wohlwill, *Z. Physik*, 1933, 80, 67).

O. R. F.

## MOLECULAR CONDUCTIVITY.

### DEFINITIONS.

Electrical conductivity or "conductance" is defined as the reciprocal of resistance, and thus has the units  $\text{ohm}^{-1}$  (sometimes called "mhos").

Specific conductivity ( $\kappa$ ) is the reciprocal of specific resistance (resistivity) and is therefore the current which passes between the opposite faces of a unit cube of the material under an applied potential difference of 1 v. If  $R$  is the resistance between two parallel faces of area  $A$ , and distance  $l$  apart, the specific resistance is  $RA/l$  and the specific conductivity  $\kappa = l/RA$ . (Units of  $\kappa$ :  $\text{ohm}^{-1} \text{ cm.}^{-1}$ ).

Equivalent conductivity ( $\Lambda$ ) is defined as  $\kappa V$ , where  $V$  is the volume in ml. containing 1 gram-equivalent of solute. Hence

$$\Lambda = 1,000\kappa/C$$

where  $C$  is the concentration in gram-equivalents per litre.

Molecular conductivity ( $\Lambda_m$ ) is defined as  $\kappa V_m$  where  $V_m$  is the volume in c.c. containing 1 gram-molecule of solute. Hence

$$\Lambda_m = 1,000\kappa/m$$

where  $m$  is the concentration in gram-molecules per litre.  $\Lambda$  and  $\Lambda_m$  are clearly identical for uni-univalent electrolytes, and are otherwise related by a simple integral factor.

### EXPERIMENTAL DETERMINATION OF ELECTROLYTIC CONDUCTIVITIES.

Although electrolyte solutions obey Ohm's Law, their resistance cannot be measured by the usual methods employed for electronic conductors, owing to the back e.m.f. of polarisation which is set up when a current is passed. Instead, a Wheatstone bridge with an alternating current source is used, and the balance point is detected as the point of minimum sound in a telephone receiver. Fig. 1 shows the circuit used.

The source of alternating current,  $C$ , should have a frequency of about 1,000 cycles per second and may be a small induction coil or "reed hummer," but is preferably a valve oscillator since this produces the most nearly perfect sine-wave potential without a unidirectional component. Any polarisation induced during one half-phase is then exactly reversed by the second half. For precision work the telephone receiver,  $B$ , should be tuned to the frequency of the oscillator, and a one- or two-stage valve amplifier is commonly added to increase the sensitivity. For industrial purposes

it may be necessary to use an alternating-current galvanometer, or rectifier and amplifier circuit with a direct-current galvanometer.

The conductivity cell,  $A$ , should consist of rigid platinum electrodes sealed in a vessel of silica or resistance glasses such as "Pyrex"; ordinary soft glass gives off too much alkali. For general purposes the design of the cell is not critical, and a great variety of forms have been used, such as the bottle type, dipping, and pipette cells, but for work of high precision special cells must be used which are designed for rigidity, exclusion of air, absence of electrical errors, etc. Washburn (*J. Amer. Chem. Soc.*

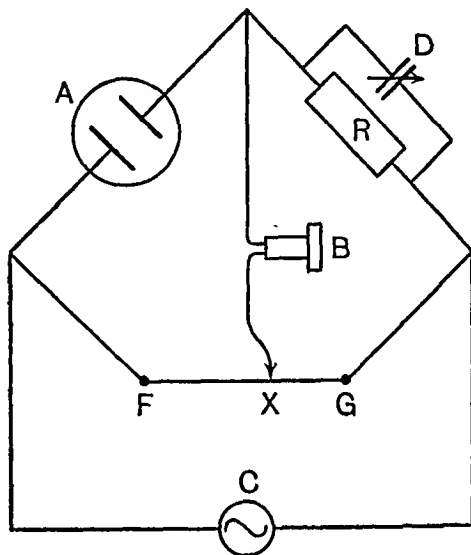


FIG. 1.—DIAGRAM OF WHEATSTONE BRIDGE FOR MEASURING ELECTROLYTIC CONDUCTIVITY.

A, Conductivity cell; B, telephone; C, alternating-current source; FG, slide wire; R, calibrated variable resistance; D, variable condenser.

1916, 38, 2431) designed a number of cells to cover different conductivity ranges. (*See also* Ives and Riley, *J.C.S.* 1931, 1998; Jones and Bollinger, *J. Amer. Chem. Soc.* 1931, 53, 411.) Shedlovsky (*ibid.* 1932, 54, 1411) used a special form of cell for extremely dilute solutions. Conductivity cells must, of course, be cleaned and washed very thoroughly. The electrodes are generally platinised by electrolysis in a solution containing 3 g. of chloroplatinic acid and 0.02–0.03 g. of lead acetate dissolved in 100 ml. of water; the object is to reduce polarisation by facilitating reversibility. It is not desirable to platinise electrodes for use with very dilute solutions, owing to adsorption by the platinum black. Conductivity is very sensitive to temperature, and the cell must therefore be placed in a thermostat, preferably of oil.

Since the dimensions of conductivity cells are rarely known exactly, it is usual to determine the effective "cell constant" by measuring the resistance of the cell when it contains a salt solution of accurately known specific conductivity. Aqueous potassium chloride solu-

tions are generally used. Table I summarises some of the very accurate measurements of Jones and Bradshaw (*ibid.* 1933, 55, 1780).

TABLE I.—THE SPECIFIC CONDUCTIVITY OF AQUEOUS POTASSIUM CHLORIDE SOLUTIONS.

Concentration.		Specific conductivity (ohm <sup>-1</sup> cm. <sup>-1</sup> ).		
Normality.	G. of KCl per kg. of solution, in vacuum.	0°C.	18°C.	25°C.
1.0	71.1352	0.06518	0.09784	0.11131
0.1	7.41913	0.007138	0.011167	0.012856
0.01	0.745263	0.0007730	0.0012205	0.0014088

The resistance,  $R$ , is generally a "decade box" reading from 1 to  $10^4$  ohms, the coils of which should be non-inductively wound. The variable (air) condenser,  $D$ , is placed in parallel with  $R$  to improve the sharpness with which the bridge can be balanced, and is adjusted experimentally to give the best balance point in each case. The slide-wire,  $RG$ , may be a simple metre wire, but for convenience the wire is often mounted on a cylindrical drum, and additional fixed resistances each equal to  $\frac{1}{4}$  times the resistance of  $RG$  can be connected at each end to increase the range and precision of the reading.

To carry out a measurement, the slide-wire contact  $X$  is set at about the mid-point of the wire and the resistance  $R$  and condenser  $D$  are adjusted to give the sharpest obtainable minimum of sound in the telephone. The final balance is obtained on the slide-wire. When the bridge is balanced the resistance of the cell  $A$  is given by  $R \times RX/GX$ .

The apparatus described above would suffice for the measurement of conductivities with an accuracy of about 0.1%. However, greater precision (better than 0.01%) is possible with special bridge design, including earthing and screening devices to avoid reactance errors, special technique in the preparation of standard solutions (*cf.* Frazer and Hartley, *Proc. Roy. Soc.*, 1925, A, 109, 351), calibration of slide-wire and standard resistances, and very accurate temperature control, together with the use of mercury-cup connectors to avoid thermal conduction from the cell by the leads. For details of precision methods the reader is referred to the original papers quoted, and also the following: Morgan and Lammert, *J. Amer. Chem. Soc.* 1926, 48, 1220 (contains a review of earlier work); Jones and Josephs, *ibid.* 1928, 50, 1049; Jones and Bollinger, *ibid.* 1929, 51, 2407; Shedlovsky, *ibid.* 1930, 52, 1793. For a precision bridge incorporating modern methods, see Luder, *ibid.* 1940, 62, 89.

**Purification of the Solvent.**—For all but the roughest work, solvents used for conductivity measurements must be purified with extreme care, especially when very dilute solutions are to be studied. Each solvent requires special consideration, but only water will be discussed here. Ordinary laboratory distilled water generally has  $\kappa = 2 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> or more. Com-

pletely pure water should have  $\kappa = 0.04 \times 10^{-6}$  at 18°C.; Kohlrausch and Heydweiller (*Ann. Phys. Chem.* 1894, [iii], 53, 209) obtained a small sample of water of this purity by repeated distillation under reduced pressure. However, "conductivity water," generally used, has  $\kappa$  about  $0.8 \times 10^{-6}$ . Such water can be obtained in one distillation by condensing pure steam (from a boiler containing water treated with potassium bisulphate or potassium permanganate and alkali) in a tin tube up which a current of carbon-dioxide-free air is passed. Good purification can also be effected by condensing only 80% of the steam. (For examples of conductivity stills, see Kraus and Dexter, *J. Amer. Chem. Soc.* 1922, 44, 246; Bourdillon, *J.C.S.* 1913, 103, 791; Stuart and Wormwell, *ibid.* 1930, 85.)

Good conductivity stills may produce water of  $\kappa = 0.1 \times 10^{-6}$  or even less, but such water rapidly absorbs carbon dioxide when exposed to air, and its conductivity rises to about  $0.8 \times 10^{-6}$ . This is known as "equilibrium water" and is commonly used for measurements. Water with low conductivity can be kept for long periods in closed vessels of resistant glass without much increase of conductivity.

The question of applying a correction to conductivity measurements to allow for the residual conductivity of the solvent is intricate, as the correction depends on the nature of the impurities present and the solute being studied (*see* C. W. Davies, "The Conductivity of Solutions," Chapman and Hall, London, 1929, Chap. IV; Wynne-Jones, *J. Physical Chem.* 1927, 31, 1647).

#### EXPERIMENTAL RESULTS.

The conductivities of a very large number of solutions have been determined. The classic work of Kohlrausch still remains the chief bulk of reliable data, except for some recent accurate measurements in very dilute solutions. For detailed numerical results, *see* the Landolt-Börnstein "Physikalisch-Chemische Tabellen."

**Aqueous Solutions.**—It is well known that conductivity data show that solutes in aqueous solutions can be divided roughly into three broad classes—non-electrolytes (*e.g.*, urea, sucrose, etc., solutions of which are no more conducting than pure water), weak electrolytes (*e.g.*, organic acids and bases), and strong electrolytes (*e.g.*, inorganic salts of strong acids and bases). However, no sharp distinctions exist, and there is a continuous transition from one class to another. Figs. 2 (a) and 2 (b) show some of Kohlrausch's results for concentrated and dilute solutions of some common electrolytes.

Although the specific conductivity ( $\kappa$ ) of solutions generally increases with increasing concentration (since more conducting particles are being added per unit volume), the increase is not proportional to the concentration increase, and consequently the equivalent (or the molecular) conductivity decreases (Fig. 2). The decrease is ascribed to two factors. Firstly, the degree of dissociation of weak electrolytes such as acetic acid and ammonium hydroxide is controlled by the Law of Mass Action (*v.* Vol. II, 536*b*; VI, 383*a*). Thus, a weak electrolyte,

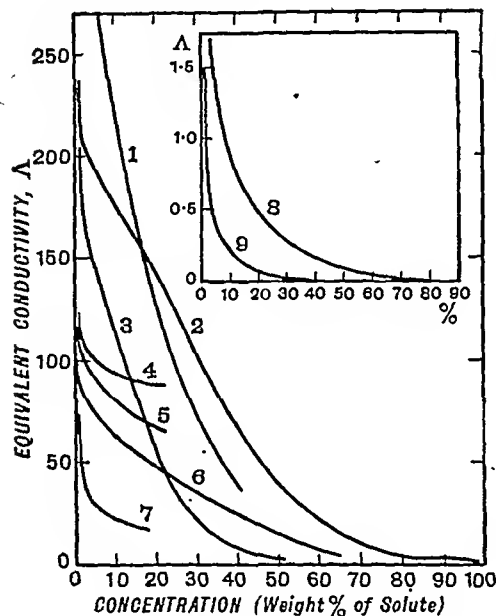
AB, dissociating into ions  $A^+$  and  $B^-$ , obeys the mass action expression:

$$a_{A^+} \cdot a_{B^-} / a_{AB} = K \quad \dots (1)$$

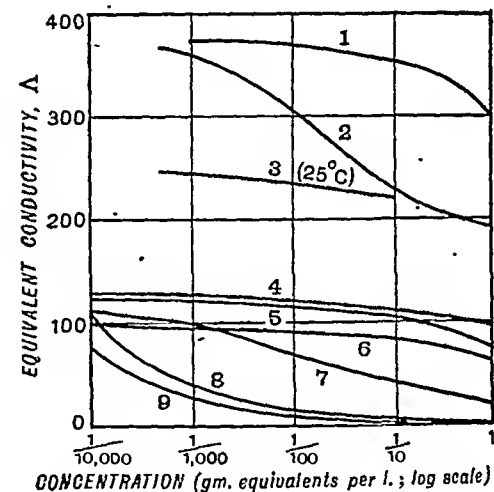
where  $a$  is the thermodynamic activity and  $K$  the "dissociation constant." For very weak electrolytes, where the total ion concentration is low, activities can be replaced by concentrations, and the classical Arrhenius theory is applicable. According to this theory the degree of dissociation is supposed to be given by the "conductance ratio,"  $\Lambda_c / \Lambda_0$  where  $\Lambda_0$  is the equivalent conductivity at infinite dilution. Combination of this with the mass-action expression (1) leads to Ostwald's Dilution Law for weak electrolytes:

$$\Lambda_c^2 \cdot c / \Lambda_0 (\Lambda_0 - \Lambda_c) = K \quad \dots (2)$$

This holds in practice as the limiting law for dilute weak electrolytes.



1(a)



(b)

FIGS. 2 (a) AND 2 (b).—EQUIVALENT CONDUCTIVITIES OF SOME CONCENTRATED (a) AND DILUTE (b) AQUEOUS SOLUTIONS AT 18°C.

1, HCl; 2,  $H_2SO_4$ ; 3, NaOH; 4, KCl; 5,  $KNO_3$ ; 6,  $CH_3COOK$ ; 7,  $CuSO_4$ ; 8,  $CH_3COOH$ ; 9,  $NH_4OH$ .

potassium nitrate in 0.1N. solution is about 96% dissociated ( $K=1.4$  g.-mol. per litre). Bivalent salts such as cupric sulphate are probably less dissociated (Cowperthwaite, Trans. Faraday Soc. 1933, 29, 593), but it should be understood that numerical values of  $\alpha$  are not known for certain, and at the present time there is no direct method of determining the degree of dissociation of salts. (For further details see H. Falkenhagen, "Electrolytes," trans. by R. P. Bell, Oxford, Clarendon Press, 1934.)

The second factor responsible for the decrease of  $\Lambda$  with increasing concentration is the electrostatic interaction between the ions. Each ion is believed to be statistically closer to ions of opposite charge than to other ions of the same charge; the immediate environment of a

Between the very weak electrolytes which are dissociated only to a slight extent ( $\alpha=0.38\%$  for N. acetic acid) and the strongest salts, such as potassium chloride, which are generally believed to be completely dissociated in dilute solutions, there is a whole range of salts which, while not consisting of covalent structures, are yet not wholly free ions. For instance, the conductivity curve of very dilute solutions of potassium nitrate is very close to that of potassium chloride [Fig. 2 (b)], but at moderate concentrations it is considerably lower [Fig. 2 (a)]. It is possible that such salts exist to some extent as "ion-pairs" even in dilute solutions. The same association phenomenon probably occurs also with even the strongest salts in concentrated solutions. Davies (*op. cit.*), following Onsager (Physikal. Z. 1927, 28, 277), deduced approximate values for the dissociation constants of salts in very dilute solutions by comparing theoretical and experimental values of  $\Lambda_c$ . According to this theory potassium chloride appears to be completely dissociated, but

positive ion is an "ion atmosphere" which is on the whole more negative than positive (and vice versa). The result is a retardation of the ion's mobility in an electric field, which leads to a decrease of  $\Lambda$  with increase of concentration. This effect, free from dissociation complications, is seen in dilute solutions of potassium chloride [Fig. 2 (b)].

The effect of interionic attraction on conductivity was treated theoretically by Debye and Hückel (Physikal. Z. 1923, 24, 185, 305, 334), who obtained an equation of the form:

$$\Lambda_0 - \Lambda_c = k\sqrt{c} \quad \dots (3)$$

The same relation had been suggested earlier, empirically, by Kohlrausch, and used by him for extrapolation purposes.



The mathematical theory has been further developed by Onsager (*ibid.* 1926, 27, 388), Fuoss (Chem. Reviews, 1935, 17, 27), Bjerrum (Det. Kgl. Danske Viden., 1926, 7, [9], 1), Kirkwood (J. Chem. Physics, 1934, 2, 767) and others. The modern theories are successful in accounting for the results for ideal electrolytes such as potassium chloride in very dilute solutions. At present neither dissociation nor ion interaction can be treated theoretically for concentrated solutions.

**Effect of Temperature and Viscosity.**—The mobility of ions (*see* MIGRATION, IONIC, this Vol., p. 92c) depends on the viscous resistance of the solvent, and consequently the  $A_0$  values of solutions in any solvent increase with increase of temperature. Kohlrausch expressed the temperature-dependence of specific conductivity by an empirical equation of the form:

$$\kappa t = \kappa_0(1 + at + bt^2) \dots (4)$$

For 5% potassium chloride,  $\kappa_0 = 455 \times 10^{-4}$ ,  $a = 274 \times 10^{-4}$ ,  $b = 71 \times 10^{-6}$ . Complex changes of conductivity with temperature are observed with some solutions, since  $A$  is affected by at least three factors—viscosity, dielectric constant, and degree of dissociation (and possibly extent of solvation also).  $A$  sometimes reaches a maximum and then falls at higher temperatures. Experimentally it is difficult to separate the different factors which are operative, *e.g.*, to change the viscosity of a solution without altering its dielectric constant.

**Non-aqueous Solutions.**—Many measurements of conductivities in non-aqueous solvents have been made, but the results are more complex and difficult to analyse theoretically than those for aqueous solutions. For experimental data *see* P. Walden, "Elektrochemie nicht-wässriger Lösungen," Leipzig, J. Ambrosius Barth, 1924; Kraus and Fuoss, J. Amer. Chem. Soc. 1933, 55, 21, 476, 1019, 2387; Goldschmidt *et al.*, Z. physikal. Chem. 1928, A, 132, 257; Barak and Hartley, *ibid.* 1933, A, 165, 272; Mead, Hughes, and Hartley, J.C.S. 1933, 1207.

In general, since most liquids have lower dielectric constants than water, electrolytes in non-aqueous solutions are far *weaker* (*i.e.*, less dissociated) and their conductivities are small. In many cases the range of applicability of the Onsager equation is in inaccessiblely dilute solutions, and often  $A_0$  cannot be determined with any accuracy. Solutions of salts in methyl or ethyl alcohol behave somewhat similarly to aqueous solutions in that  $A$  increases continuously with dilution (*cf.* Barak and Hartley, *l.c.*), but solutions in solvents of low dielectric constant often exhibit a minimum (*cf.* Kraus and Fuoss, *l.c.*). Attempts have been made to explain the results theoretically by considering the formation of neutral "ion-pairs" ( $A^+B^-$ ) which are supposed to take no part in the conduction, while at high concentrations even "triple ions" ( $A^+B^-A^+$ ) may be present (Fuoss, Bjerrum, Kirkwood). Other authors, however (*e.g.*, Gronwall, La Mer, and Sandved, Physikal. Z. 1928, 28, 358) dispense with the idea of incomplete dissociation altogether. For a review of these theories *see* Falkenhagen, *l.c.*; D. A. MacInnes, "Principles of Electro-

chemistry," New York, Reinhold Publ. Corp., 1939.

**Solids and Fused Salts.**—Most compounds in the solid state are non-conducting, but a few salts are feeble electrolytic conductors, *i.e.* the passage of current is accompanied by transport of matter according to Faraday's Laws of Electrolysis. In these solids conduction is supposed to take place by migration of ions through "holes" in the crystal lattice. The current may be carried either by the cation alone (*e.g.*,  $Ag^+$  in silver chloride), the anion alone ( $Cl^-$  in lead chloride), or both ions may move (potassium chloride). Another class of solids become *electronic* semi-conductors owing to lattice defects caused by a stoichiometric excess or deficiency of one kind of atom (*e.g.*, oxygen deficiency in zinc oxide).

The conductivity of solid electrolytic conductors increases rapidly with rise of temperature, and in many cases the molten salt is highly conducting. For example,  $\kappa$  for silver chloride is 0.0003 ( $ohm^{-1} cm.^{-1}$ ) at 250°, 0.11 at 450° (solid), 3.76 at 456° (liquid), and 4.16 at 600°C.

Biltz (Z. anorg. Chem. 1926, 152, 267) has studied the conductivity of a large number of chlorides in the liquid state, and has pointed out interesting regularities according to the position of the elements in the Periodic Table. Some chlorides, such as silicon and titanium tetrachloride, are purely covalent in structure and are perfect insulators; aluminium chloride is feebly ionic ( $A = 15 \times 10^{-6}$ ); liquid sodium chloride and silver chloride are good conductors ( $A = 135.5$  and 111.5, respectively) (*see* P. Drossbach, "Elektrochemie geschmolzener Salze," Berlin, J. Springer, 1938).

**High Potentials and High Frequencies.**—Ohm's Law is valid for electrolyte solutions under the ordinary conditions of measurement (Jones and Bollinger, J. Amer. Chem. Soc. 1931, 53, 1207), but at high potentials and high frequencies conductivities *increase*. These effects, although small, are of considerable theoretical interest (*see* H. Falkenhagen, *op. cit.*).

The *Wien effect* is the increase of conductivity observed at potential gradients of the order of  $10^5$  v. per cm. instead of the usual 1 v. per cm. The increase of  $A$  is of the order of 5% in fields of this strength (Wien *et al.*, Ann. Physik. 1927, [iv], 83, 305; 1929, [v], 1, 400; Schiele, *ibid.* 1932, [v], 13, 811).

The *Debye-Falkenhagen effect* is a similar increase which occurs when conductivities are measured at very high frequencies. For example,  $A$  for cupric sulphate is 10% greater when measured in a field alternating with a frequency of  $10^8$  cycles per second than when obtained by the usual Kohlrausch method at audio-frequency ( $10^3$  cycles per sec.) (Sack *et al.*, Physikal. Z. 1928, 29, 627; 1929, 30, 576; 1931, 31, 345; Arnold and Williams, J. Amer. Chem. Soc. 1936, 58, 2613, 2616). The effect is ascribed to the "time of relaxation" required for the ion atmosphere to adjust itself to the changes of polarity, and it appears that the experimentally observed results are in good agreement with the theoretical predictions of Debye and Falkenhagen (Physikal. Z. 1928, 29, 121, 401, 423).

## APPLICATION OF CONDUCTIVITY MEASUREMENTS.

In addition to their importance for the theory of electrolyte solutions, conductivity measurements can be usefully applied to many practical problems, including determination of solubilities of sparingly soluble salts; conductometric titrations of acids and alkalis, or titrations in which a precipitate is formed; determination of constants of dissociation and hydrolysis; and measurement of changes of concentration, for instance, in studying the kinetics of a reaction in solution. Conductivity can also be applied to many technical purposes; for example, a simple type of conductivity cell introduced into the out-flow pipe of a base-exchange water-softening plant has proved very convenient for controlling the duration of washing after regeneration by brine. Washing is continued until the conductivity falls to a particular scale reading which has been previously chosen empirically. Such conductivity methods can easily be adapted to automatic control.

J. A. K.

**MOLECULAR DEPRESSION AND ELEVATION CONSTANTS.** The freezing-points and boiling-points of a large number of solutions have been studied in order to obtain information concerning the molecular weights of solutes, their states of aggregation, activity coefficients, transition temperatures, etc.

**Freezing-point Depression.**—The addition of a small amount of solute to any liquid lowers the freezing-point of the system, and provided that crystals of pure solvent separate first on cooling (*i.e.*, eutectic formation is excluded), the depression produced is approximately proportional to the total number of molecules of solute present, and independent of their chemical nature. The depression of freezing-point produced by a solute concentration of 1 g.-mol. in 1,000 g. (or, sometimes, 100 g.) of solvent is defined as the Molecular Freezing-point Depression Constant (or Cryoscopic Constant) ( $K_f$ ), and, once known, it is useful for predicting the freezing-points at other concentrations or for determination of the molecular weight of a solute (*see* MOLECULAR WEIGHTS, DETERMINATION OF, this Vol., p. 209c). If the pure solvent freezes at  $t^\circ\text{C}$ ., the lowering produced by a solution of concentration  $C$  g.-mol. per 1,000 g. is simply:

$$-\Delta t = K_f C \quad \dots \quad (1)$$

The lowering of freezing-point arises from the fact that the partial vapour-pressure of solvent in a solution is always less than that of the pure solvent at the same temperature. At the freezing-point, solid and liquid must co-exist in equilibrium. Hence, at  $t^\circ$  the vapour-pressure of the solid is equal to that of pure solvent and greater than that of the solution. However, owing to the fact that the vapour-pressure of a solid always decreases more rapidly with decrease of temperature than that of the corresponding liquid, equilibrium can always be achieved between solid and solution at a temperature lower than  $t^\circ$ , *viz.* at the point where the solid and solution vapour-pressure curves

intersect. The lowering of freezing-point thus produced is given by:

$$-\Delta t = (RT/M L_f) \log_e (p^0/p) \quad \dots \quad (2)$$

where  $R$  = the gas constant (1.986 g.-cal. per  $^\circ\text{C}$ . per g.-mol.);

$T$  = absolute temperature ( $t + 273.1$ );

$L_f$  = latent heat of fusion of solid solvent in g.-cal. per g.;

$p^0$  = vapour-pressure of pure solvent;

$p$  = partial vapour-pressure of solution.

By assuming that Raoult's Law is applicable and that the solution is very dilute (2) can be reduced to:

$$-\Delta t = (RT/L_f) \cdot C' \quad \dots \quad (3)$$

where  $C'$  is the number of g.-mol. of solute per g. of solvent. It is more usual to express concentration as g.-mol. per 1,000 g. of solvent ( $C$ ), and hence, by comparing (3) with (1), the molecular freezing-point depression constant is obtained as  $RT/1,000 L_f$ .

In Table I are given some experimental values of  $K_f$ , obtained by extrapolating cryoscopic data to zero concentration, together with calorimetric values for  $L_f$ , and the corresponding computed values of  $K_f$ . There is no doubt that the agreement between the two values of  $K_f$  is within the experimental error. (It is notable that the data of different observers are remarkably discordant for both  $K_f$  and  $L_f$ . Data quoted are considered probable values.)

TABLE I.—MOLECULAR FREEZING-POINT DEPRESSION CONSTANTS OF SOME COMMON SOLVENTS.

Solvent.	Freezing-point, $^\circ\text{C}$ .	$L_f$ (g.-cal. per g.).	$K_f$ (calculated).	$K$ (experimental).
$\text{Br}_2$ . . . . .	-7.32	16.19	8.64	8.31
$\text{H}_2\text{O}$ . . . . .	0.00	79.67	1.859	1.853
$\text{CaCl}_2$ . . . . .	766	54.6	39	38
$\text{H}_2\text{SO}_4$ . . . . .	c.10.5	25.98	6.15	6.17
$\text{C}_6\text{H}_6$ . . . . .	5.45	29.92	5.130	5.139
$\text{H}\cdot\text{COOH}$ . . . . .	8	57.38	2.73	2.77
$\text{CH}_3\cdot\text{COOH}$ . . . . .	17	43.66	3.8	3.9
$\text{C}_6\text{H}_5\cdot\text{NO}_2$ . . . . .	5.67	22.6	6.83	6.89
$\text{o}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\text{OH}$	44.3	26.8	7.47	7.44
Palmitic acid				
$(\text{C}_{15}\text{H}_{31}\cdot\text{COOH})$	62.65	51.05	4.39	4.31
Camphor				
$(\text{C}_{10}\text{H}_{16}\text{O})$ . . . . .	178	10.7	38	40.0

The above simple relationships are valid only for extremely dilute solutions of "normal" solutes—the so-called "ideal solutions." At appreciable concentrations real solutions exhibit marked deviations. If the solute associates or dissociates the freezing-point depression is approximately determined by the total number of molecular individuals present in the solution, and hence the freezing-point has been used to estimate the degree of association or dissociation. The other cause of non-ideality is the fact that concentration is not a true measure of thermodynamic activity for any except the most dilute solutions. Activity coefficients of non-



electrolytes in dilute solutions do not differ greatly from unity, but this is far from the case with electrolytes. Consequently, freezing-point depression curves of electrolytes in dissociating solvents are complex. Some data for  $-\Delta t/C$  for a number of aqueous solutions are shown in Fig. 1.

Cryoscopic measurements are commonly used to obtain approximate molecular weights and activity coefficients. For the former purpose, Rast's micro-method, which utilises the high  $K_f$  value of camphor, is of special interest. Other substances with high cryoscopic constants have been studied by Pirsch (Ber. 1935, 68 [B], 67). Chadwell and Politi (J. Amer. Chem. Soc. 1938, 60, 1291) calculated activity coefficients of urea, urethane, and acetamide in aqueous solution from freezing-point depressions,

**Elevation of Boiling-point.**—The boiling-point of any liquid is raised by the addition of a less volatile solute, owing to the lowering of total vapour-pressure. By assuming Raoult's Law and combining it with the Clausius-Clapeyron equation, an expression is obtained for the boiling-point elevation which is formally identical with that for the freezing-point depression, except for the sign, viz.:

$$\Delta t = (RT/1,000L_v) \cdot C = K_b C$$

where  $T$  is the boiling-point,  $L_v$  the latent heat of vaporisation per g., and  $K_b$  the Molecular Boiling-point Elevation Constant (or "Ebullioscopic Constant"), defined as the elevation of boiling-point of an ideal solution of concentration 1 g.-mol. per 1,000 g. of solvent.

Table II gives data for boiling-point,  $L_v$ ,  $K_b$  (experimental), and  $K_b$  (calculated) for some common solvents.

As with  $K_f$ , values of  $K_b$  calculated from calorimetric determinations of  $L_v$  agree, within the experimental error with the values of  $K_b$  obtained by extrapolating ebullioscopic measurements to infinite dilution.

Boiling-point elevations of real solutions deviate from the simple theory in the same ways as mentioned above for freezing-point depressions, but to a much greater extent, not only because of the greater experimental errors usually incurred, but also on account of the high

vapour-pressures involved, which introduce deviations from the ideal-gas laws. For these reasons, boiling-point measurements are far

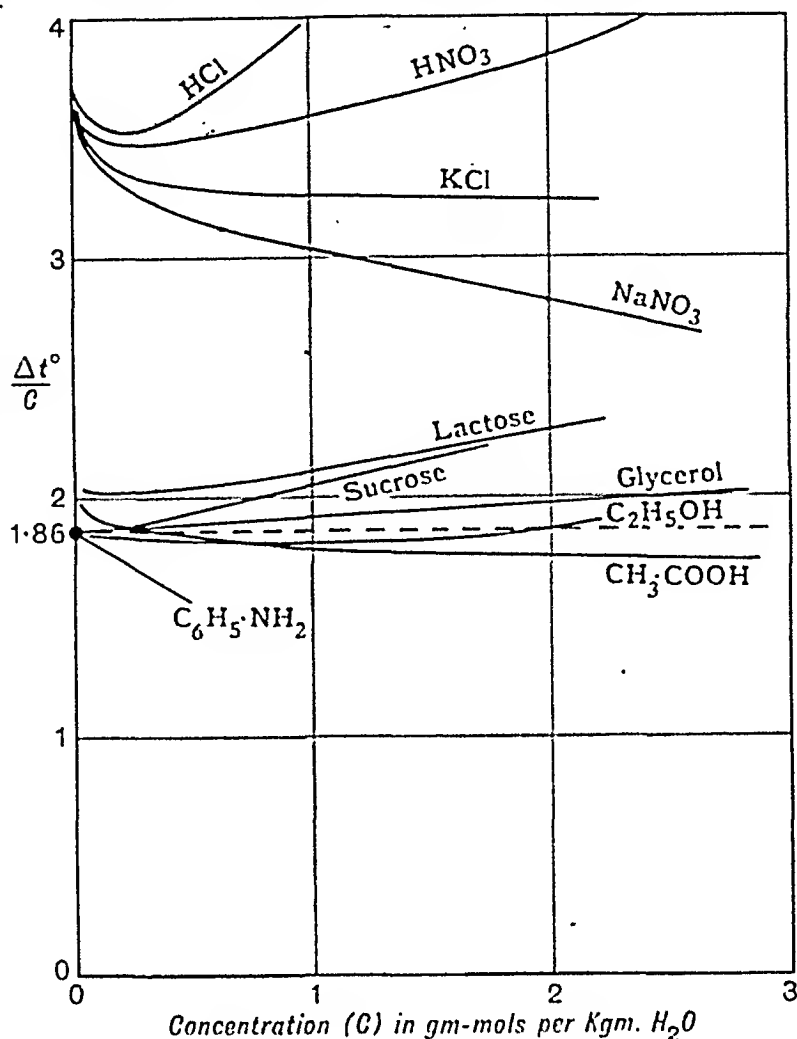


FIG. 1.—FREEZING-POINT DEPRESSIONS OF SOME AQUEOUS SOLUTIONS.

less reliable and useful than freezing-point determinations for studying physico-chemical problems.

Rosanoff and Duuphy (J. Amer. Chem. Soc.

TABLE II.—MOLECULAR BOILING-POINT ELEVATION CONSTANTS OF SOME COMMON SOLVENTS.

Solvent.	Boiling-point, °C.	$L_v$ (g.-cal. per g.).	$K_b$ (calculated).	$K_b$ (experimental).
$\text{Cl}_2$ . . . . .	-33.6	67.4	1.69	1.65
$\text{Hg}$ . . . . .	357	67.8	11.6	11.4
$\text{H}_2\text{O}$ . . . . .	100.0	539.6	0.512	0.521
$\text{C}_6\text{H}_6$ . . . . .	80.2	94.98	2.61	2.61
$\text{CHCl}_3$ . . . . .	61.2	58.4	3.80	3.88
$\text{CCl}_4$ . . . . .	76.7	46.4	5.24	5.29
$\text{CS}_2$ . . . . .	46.3	87.7	2.34	2.29
$\text{C}_2\text{H}_5\text{OH}$ . . . . .	78.4	204.0	1.21	1.20
$(\text{C}_2\text{H}_5)_2\text{O}$ . . . . .	34.6	83.9	2.14	2.16
$(\text{CH}_3)_2\text{CO}$ . . . . .	56.3	125.28	1.720	1.725

1914, 36, 1411) showed that Molecular Boiling-point Elevation Constants can be calculated *directly* from vapour-pressure data by applying the Duhem-Margules equation. This gives:

$$K_b = p^0 M / 1,000 (dp^0/dT) \quad (4)$$

The dependence of the vapour-pressure of a liquid on temperature ( $dp^0/dT$ ), is generally known more accurately than  $L_v$ , and consequently  $K_b$  calculated from (4) is likely to be more reliable than the calorimetric value, or even the direct ebullioscopic value. According to Hoyt and Fink (J. Physical. Chem. 1937, 41, 453) equally good results are obtained from the usual expression, provided that gas imperfections are corrected by means of the Berthelot equation. These authors found that the average increase of  $K_b$  for an increase of atmospheric pressure of 1 mm. was 0.25.

J. A. K.

#### MOLECULAR DISTILLATION.\*

During the past fifteen years short-path high-vacuum distillation has received considerable attention from reviewers and bibliographers, but has not found wide application in the laboratory and industry. The reason for the laboratory neglect is the vagueness of the method; separations are neither complete nor exact unless much complicated apparatus is assembled, and it is just this complexity that the organic chemist distrusts. The application to industry has been delayed pending the development of large, economical stills and vacuum pumps. These are now in sight and at the time of writing (1944), liquids of high molecular weight are being distilled at the rate of many millions of pounds annually.

Of the bibliographies, the most important and complete have been issued by the U.S. Regional Soybean Industrial Products Laboratory, Urbana, Illinois,<sup>1</sup> whence a fine set of abstracts has also come from the pen of Samuel B. Detwiler, jun.<sup>2</sup> More than a dozen reviews have appeared, the more important being contained in the symposium appearing in the Journal of the Society of Chemical Industry, 1939,<sup>2a</sup> in Alexander's "Colloid Chemistry,"<sup>3</sup> and in Chemical Reviews,<sup>11</sup> the latter, however, being confined chiefly to the work of the present author's laboratory. Parallel with these reviews are about a score of papers by Burch,<sup>4</sup> Waterman,<sup>5</sup> Fawcett,<sup>6</sup> and others<sup>7</sup> describing or advocating particular methods of high-vacuum distillation. The writer's first statement of methods appeared in 1930<sup>8</sup> and was restated in 1932<sup>9</sup> and 1935, greatly amplified in 1937,<sup>10</sup> and progressively restated in 1940, 1941, 1943, and 1944.<sup>11</sup> The present review bears an inevitable similarity to the more recent of these articles.

#### INDUSTRIAL APPARATUS.

The short-path still in its simplest form is a flat vessel with a heated floor, cooled ceiling, and a "perfect" vacuum in between. Molecules evaporating from liquid resting on the bottom condense on the ceiling without obstruction from

pipings or molecules of foreign gas. Distillation thus occurs at the lowest possible temperature.

Heavy petroleum residues,<sup>12</sup> glyceride oils, and the oil-soluble vitamins typify the distillands that have controlled the design of short-path, high-vacuum stills. The first comprehensive attempt to purify organic substances on an industrial scale by short-path distillation was made by C. R. Burch<sup>13</sup> and collaborators at Metropolitan Vickers.<sup>14</sup> The stills were made of metal and were evacuated by metal condensation pumps operated with a phlegmatic hydrocarbon oil<sup>13</sup> instead of mercury, which previously had been in universal use. Two important early types of stills were the cascade-tray still and the falling-film still.<sup>15</sup> The working elements of the cascade-tray still are shown in Fig. 1. Here the hot trays A are mounted on a heated central tube B above a collecting gutter C for spent distilland. The assembly is housed

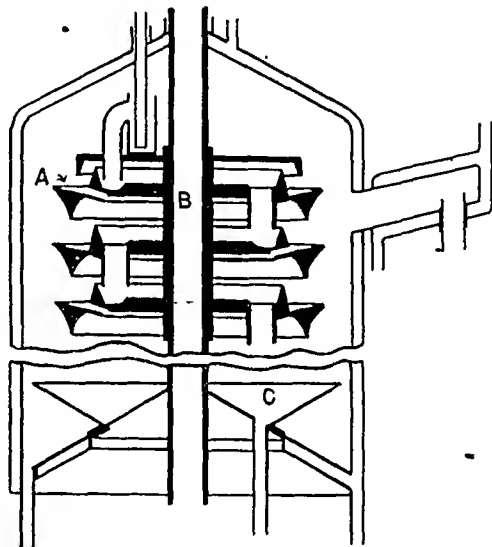


FIG. 1.—CASCADE-TRAY STILL OF BURCH AND BANCROFT.

within a double-walled vacuum-tight chamber which serves as the condenser. An advantage of this kind of still was the good mixing of the spent surface layer with unexposed underlayers of the distilland as it streamed from tray to tray. An occasional disadvantage was the relatively large quantity of distilland held in the still, with consequent long exposure to heat.

A commercial falling-film still was developed and operated at Distillation Products, Inc., Rochester, New York, for over five years. Each unit comprised five columns and a degasser, situated one above the other on five mezzanine floors, the lowest of which, with fifth column and control panels for all the columns, is shown in Fig. 2. The columns were made of mild-steel tubing with a spiral pattern embossed on the outside to aid in spreading the distilland. They were about 4 ft. high and were covered with large Pyrex glass domes, the combination standing on a hollow base which was connected to a pair of horizontal *fractionating*<sup>16</sup> condensation pumps. The back of one can be seen

\* Communication No. 59 from the Laboratories of Distillation Products, Inc., Rochester 13, New York, U.S.A.

facing the observer. Over half a million gallons of fish-liver oil were passed through this equipment before the falling-film type of still was superseded.

The falling-film column provides a simple and elegant evaporator for a molecular still. The defects of the early patterns were due to the properties of oils exposed to a very high temperature on one side and a cold condenser on the other, the combination causing nearly uncontrollable surface-tension movements. The oil gathers into ridges and becomes detached from the column, which in turn becomes overheated and soiled with carbon. An example of

channelling and subsequent carbonisation is shown in Fig. 3. The effects can be minimised by using a heated circulating fluid instead of electrical heat, and by repeated redistribution of the distilland.<sup>17</sup> There are, however, other types of surface evaporators with which the distilland can be brought into complete subjugation.<sup>18</sup>

The molecular evaporator receiving chief contemporary development is a heated rotor<sup>19</sup> which uses centrifugal force to spread the distilland and keep it flattened during distillation. An early laboratory model (1935) of a centrifugal high-vacuum still employed an



FIG. 2.—INDUSTRIAL FALLING-FILM STILL. GLASS DOME ON THE LEFT COVERS THE FIFTH EVAPORATOR IN A SUCCESSION OF INDIVIDUAL STILLS. THE PANELS FOR CONTROLLING TEMPERATURE AND PRESSURE ARE SHOWN ON THE RIGHT.

aluminium plate 6 in. in diameter, spun into a cone embracing about 130°. The cone was warmed by radiant heat, and the distilland was led to the centre by a glass tube and collected from the rim by a water-cooled stationary gutter. A water-cooled plate or perforated grid<sup>20</sup> was mounted as a condenser in front of the rotor, and the whole assembly was enclosed in a glass dome, illustrated in Fig. 4 with the internal condenser removed. A cross-sectional diagram is shown in Fig. 5; small industrial installations are pictured in Figs. 6 and 7, the former with covers removed. The largest rotary evaporators so far constructed accommodate 700–1,000 lb. of oil per hour at 250°C. and a residual gas pressure of 10<sup>-3</sup> mm.

#### INDUSTRIAL PROCESSES.

The two uses for the molecular still which first appealed to industrialists were in the distillation of petroleum residues,<sup>12</sup> and of glyceride stand-oils.<sup>21</sup> Though neither use has materialised to any extent, the experience gained from their early exploration has been invaluable in the vitamin field, and there is now some prospect that the benefit will be reflected back to the original objective as the vitamin stills become capable of larger, more economical operation. Even so, occasional patents in short-path distillation are issued to petroleum companies<sup>22</sup>; and the manufacture of "Apiezon" high-vacuum oils and greases<sup>23</sup> continues on a significant, if miniature, scale.

In the "stand" or drying-oil field, pioneer work was done by Waterman<sup>24</sup> in Holland and Imperial Chemical Industries, Ltd.,<sup>25</sup> in England, followed by Morse<sup>26</sup> and his successors at Distillation Products, Inc. The process consists in improving the drying qualities of an oil before or after bodying. Three variants are found to be practicable:

1. The sterols, tocopherols,<sup>27</sup> and other trace substances which are valuable separately but detrimental to a drying oil are "stripped" off by passing the oil at relatively low temperature through the short-path still.

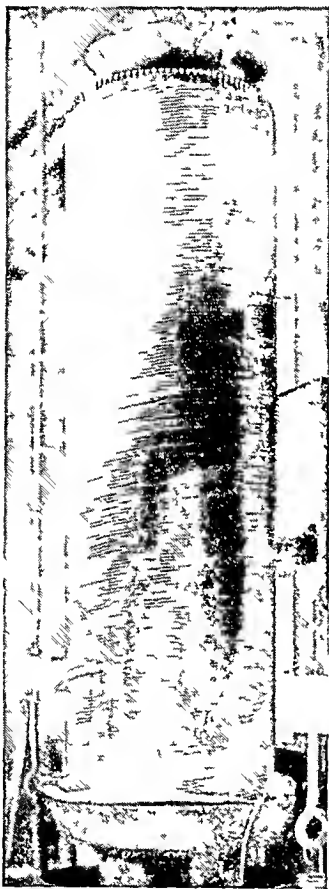


FIG. 3.—FALLING-FILM STILL COLUMN, SHOWING CHANNELLING AND SUBSEQUENT CARBONISATION AFTER TWO DAYS' OPERATION.

2. The lower molecular-weight, more saturated glycerides are distilled off, leaving a residue with improved bodying and drying characteristics.
3. A drying oil is bodied and then passed through the molecular still to remove the unbodyed fraction. There results a rapidly drying oil of superior hardness.

Processes of the above type have been worked out in considerable detail for linseed and sardine oils, which can yield vehicles for paints and varnishes equal to perilla or dehydrated castor

oil in most respects, except perhaps in resistance to alkaline liquids. That such processes have not yet been commercialised is due to the lack of economical stills and the difficulty of securing new equipment in war time.

**Oil-soluble Vitamins.**—Vitamin-A and now vitamin-E have provided the occasion, the incentive, and the wherewithal which has covered practically the entire development of molecular distillation to date—an investment of some millions of dollars—and at a profit. In chronological order may be noted the laboratory distillation of natural vitamin-A esters<sup>15</sup> directly from fish-liver oils; the industrial distillation of vitamin-A-alcohol<sup>28</sup> from the solvent extract of saponified fish livers and fish-liver oil; and the industrial distillation of vitamin-A esters from fish-liver oils<sup>30</sup>. It is the latter development which employs the stills

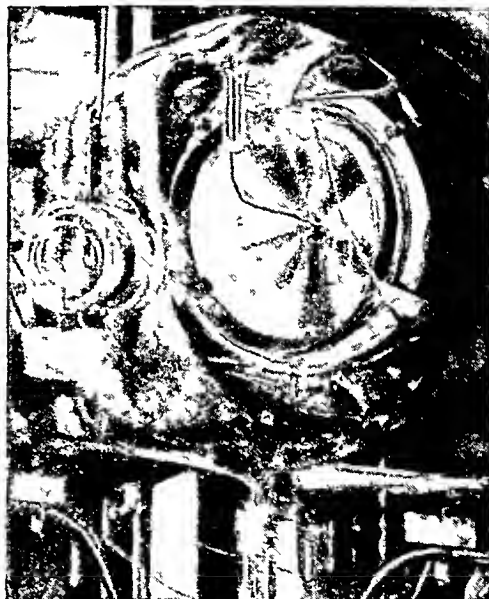


FIG. 4—EARLY CENTRIFUGAL PLATE STILL. THE OIL IS FED THROUGH THE GLASS TUBE TO THE CENTRE OF THE PLATE, WHENCE IT TRAVELS OUTWARDS TOWARDS THE STATIONARY, COOLED COLLECTING GUTTER. THE CONDENSER HAS BEEN REMOVED TO GIVE A BETTER VIEW OF THE EVAPORATOR.

pictured in Figs. 6 and 7 and others since designed.

The distillation of vitamin-A, freed from fish livers by saponification, has a double significance in that it was the first successful commercial application of the molecular still, and the first operation giving nearly pure vitamin-A.<sup>31</sup> Indeed, it was from a distillate of this type that the pure crystalline vitamin<sup>32</sup> was eventually prepared.

The process for distilling vitamin-A esters directly from fish-liver oil involves the following steps:

1. Selection and blending of raw fish-liver oils to a distilland of approximately constant potency.

istry there is a steady yearly growth in the molecular weight of substances handled. Plasticisers, resins, and polymers of heavier varieties are continually introduced. Most manufacturing processes involve the simple reaction  $A + B \rightleftharpoons AB$ , as a final stage. The properties of  $AB$  are largely modified by traces of  $A$  and  $B$ , so that it becomes desirable to remove them from the finished product. The molecular still is able to strip  $A-B$  from  $AB$ , leaving the latter for use as such or ready for further treatment by distillation at a higher temperature.

**Distillation of Solids.**—Devices described in the patent literature<sup>46</sup> have not yet reached commercial development, except perhaps for an

ingenious mechanically scraped condenser due to Fawcett.<sup>47</sup>

#### THE MOLECULAR STILL IN THE LABORATORY.

The invention of the molecular still has been epitomised as "the application of the condensation pump to the surface evaporator." However, a tool that has exerted an even greater influence than the condensation pump is the modern rotary oil vacuum-pump which has replaced or augmented the water aspirator.

Very excellent small-scale distillations can be done by placing a gram of crude material in a modified test tube (Fig. 8) fitted with a short,

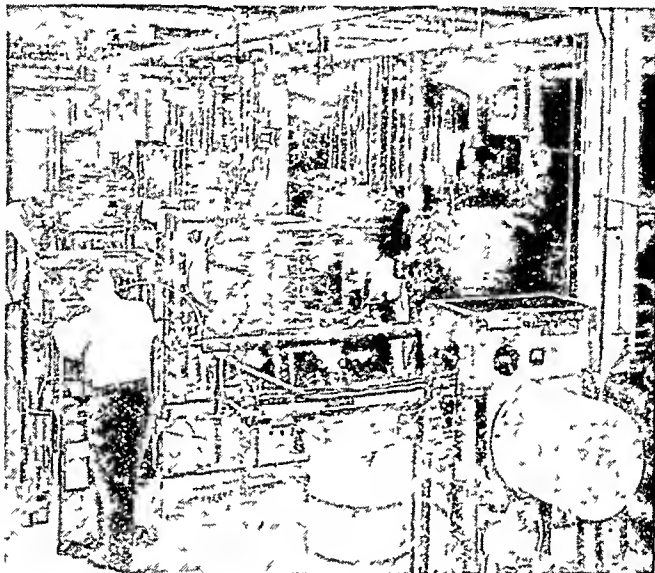


FIG. 7.—INSTALLATION OF LARGER INDUSTRIAL CENTRIFUGAL STILLS; USED CHIEFLY FOR THE SEPARATION OF VITAMIN-A ESTER CONCENTRATES FROM FISH-LIVER OIL.

length of wide-bore rubber pressure-tubing which is attached to the rotary oil-pump (the well-known "Hyvac," for instance). If the oil in the pump has been freshly replaced, the pressure in the test tube should fall to 8–10 $\mu$ . (1 $\mu$ . = 0.001 mm.), below which, in apparatus of this size, it is unimportant to go to achieve distillation at the lowest possible temperature. The distillate collects in the upper part of the tube. This kind of still in various stages of elaboration has been used to purify calciferol, vitamin-K, and the sterols.

Next in order is the true molecular pot-still, described at some length in Vol. II of the Supplement to the Third Edition of this Dictionary (1935). Present-day pot-stills are generally made in two parts<sup>48</sup> so that the condenser can be removed for cleaning; or evaporator and condenser are housed under a bell jar. Many such stills may be arranged as a permanent installation, deriving their vacuum from a common manifold. Various types of pot-stills are shown in Fig. 9.

The distillation of solids does not generally effect useful separations,<sup>43</sup> so that molecular distillation is confined chiefly to liquids and

solids dissolved in them. Here the falling-film or centrifugal evaporator gives the best separations.

Two standard types of falling-film still have come into general adoption. The first uses a glass central column, heated by electricity or thermostatically controlled fluid, which is housed in a glass tubular condenser cooled by a water jacket or an air blast. Many such stills may be arranged in series, the assembly being facilitated by standardised glass joints. Vapour pumps and condensation traps are provided for each unit, though they, and the preliminary degassing bulb, may be manifolded to a single large source of fore-vacuum. An elegant design of this type was furnished to Schott of Jena by Fawcett.<sup>6</sup> Waterman, earlier, and Detwiler<sup>49</sup> and others, later, have offered their preferred variations.

The other type of laboratory molecular still is the "cyclic-batch" still,<sup>10</sup> and we should state frankly that it has displaced other kinds in our own work. Here the evaporator may be a falling-film column or a small centrifugal evaporator connected to two reservoirs for the distilland. A mechanical or magnetic pump

circulates the distilland backwards and forwards over the evaporator from one reservoir to the other, throughout the process of distillation. In this way one highly specialised unit, complete with temperature controls, vacuum gauges, and vacuum and circulatory pumps, can serve in turn the functions of solvent stripper, degasser, and multi-column still. Two varieties of still are shown in Figs. 10 and 11, but the reader is

referred for details to descriptions which have been published so many times previously.

All distillations should provide guiding signs, otherwise the operator cannot properly control the process. The signs in ordinary distillation are the percentage distilled and the boiling-point, where temperature and pressure intersect, it being assumed that the pressure of distilling vapour coincides with that of the residual atmo-

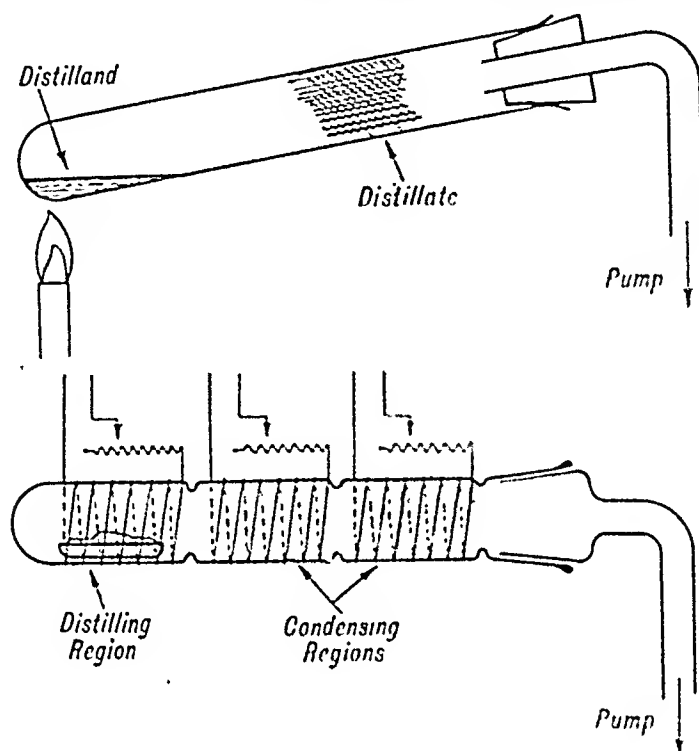


FIG. 8.—MODIFIED TEST-TUBE DISTILLATION APPARATUS.

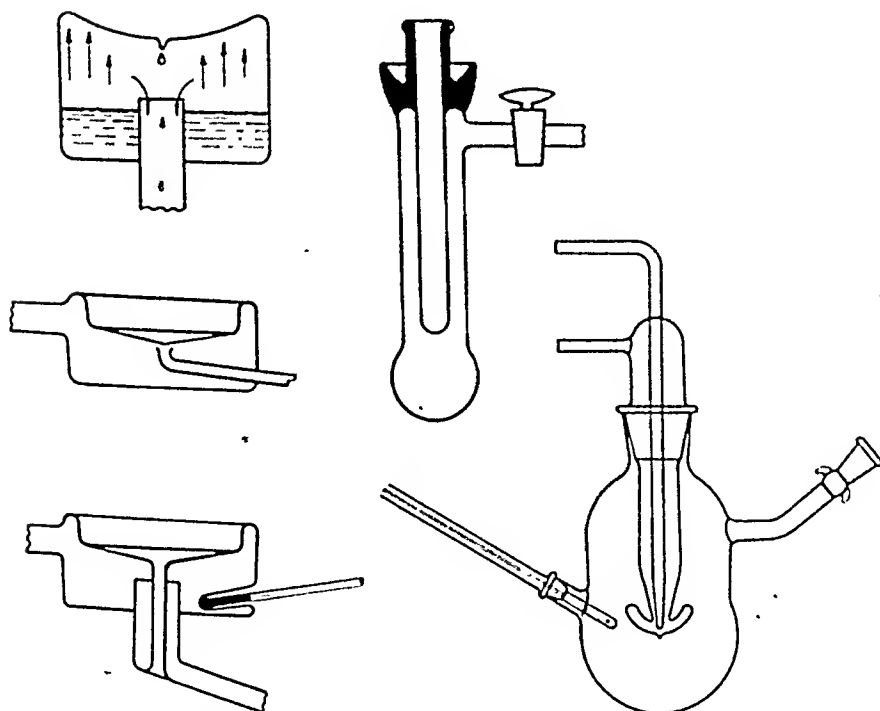


FIG. 9.—SELECTION OF GLASS POT-STILLS.

sphere—760 mm., 10 mm., etc.—in communication with the still. In the molecular still there is, by definition, no atmosphere, and there is no boiling-point, distillation occurring in some degree whenever there is a difference of temperature between evaporator and condenser. The significant variable is now *time* instead of pressure—the clock replaces the manometer and the rate of boiling must be measured at each temperature. This important difference was pointed out by Burch.<sup>4</sup>

These considerations have led to a highly conventionalised technique<sup>51</sup> of distillation in which a fixed time and a fixed rise of temperature are allotted for each cycle of the distilland, corresponding with each change of receiver. For instance, 100 ml. of oil will be placed in the still and degassed by circulating for a couple of hours over a column heated to 80°C. The individual cycle will then be adjusted to, say, exactly 10 minutes, the temperature raised to 120°, and the first fraction collected. The temperature is then raised to 130°, the receiver changed, and the distilland again cycled during exactly 10 minutes. This procedure is repeated until all has distilled—say 12 times, until the temperature reaches 240°C. In these circumstances it is found that given constituents always occur in maximum relative concentration at the same temperature, so that they may be recognised by the temperatures at which they appear. The peaks of their *elimination curves* are an excellent substitute for ordinary boiling-points.

The underlying logic of this technique has been explained elsewhere, together with the practical details of "pilot dyes,"<sup>52</sup> "constant yield,"<sup>53</sup> and "residue" oils needed to carry out the distillation conveniently. It will suffice to say here that the method which, incidentally, has not yet been widely adopted has revealed:

That vitamin-A occurs in fish oils as  $C_{16}$ ,  $C_{20}$ , and  $C_{22}$  esters.<sup>54</sup>

That vitamin-A occurs in the liver of the rat as  $C_{16}$  ester only.<sup>55</sup>

That vitamins- $A_1$  and  $-A_2$  distil at substantially the same temperature, and probably have the same number of carbon atoms.<sup>56</sup>

That vitamin-D occurs equally in free and esterified conditions; there is more than one free form of vitamin-D in cod-liver oil.<sup>57</sup>

That vitamin-E occurs in free and bound conditions in soybean oil.<sup>58</sup>

That carotene occurs in palm oil in free condition and not bound, as formerly supposed.\*

That vitamin-A occurs in the intestines of fish as the ester, and is rapidly hydrolysed on storage of the dead gut.<sup>58</sup>

That *kifol*, a new provitamin-A, was discovered in whale-liver oil by quantitative molecular distillation.<sup>59</sup>

\* Unpublished data from the Laboratories of Distillation Products, Inc.

### Researches with the Molecular Still.—

Although quantitative distillations are often necessary, or at least desirable, to point the way, the great bulk of molecular distillation is done qualitatively in simple apparatus. The purpose, whether consciously recognised or not, is to secure a partial concentration of the substance under examination so that means of further concentration or reagents hitherto unsuccessful can be applied profitably. Using the still in this manner, Dam in Denmark and Almquist in America conducted researches on vitamin K<sup>42</sup> and other antihæmorrhagic substances.

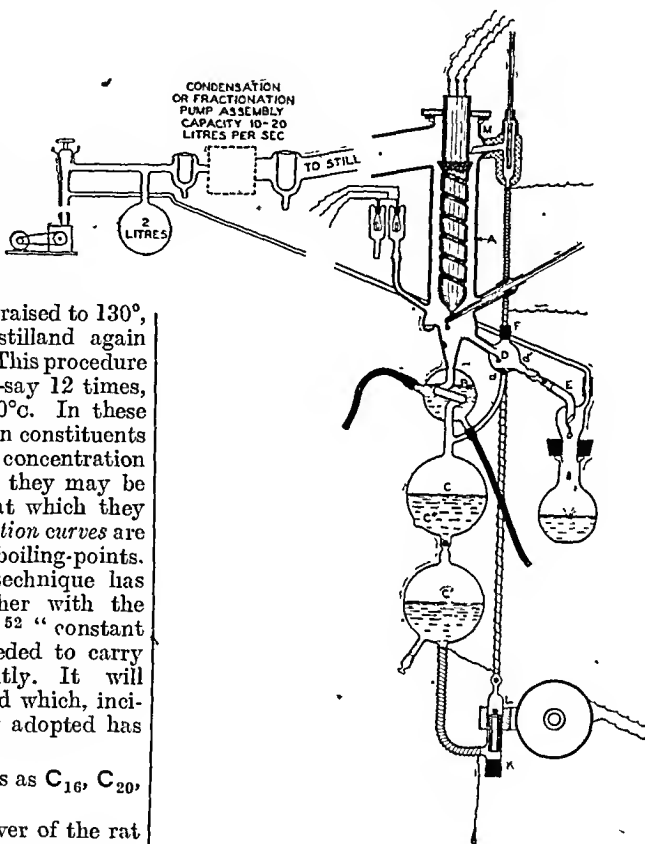


FIG. 10.—DIAGRAM SHOWING ESSENTIAL PARTS OF CIRCULATING MOLECULAR STILL.

Emerson separated  $\gamma$ -tocopherol from natural sources, Farmer and Van den Heuvel<sup>60</sup> separated docosahexaenoic acid from cod-liver oil, and Embree and Shantz<sup>61</sup> separated anhydro-vitamin-A from fish-liver oil, and obtained such derivatives as isoanhydro-vitamin-A, subvitamin-A, etc., and kifol,<sup>59</sup> from whale-liver oil. Bömer and Hüttig<sup>63</sup> separated the fats of babassu oil, Waterman and later the writer separated pure  $\beta$ -carotene from palm oil,<sup>64</sup> Rawlings<sup>35</sup> analysed soybean oil, Kass and Burr purified linolenic acid,<sup>65</sup> Johnston and Bradley fractionated dimers of methyl esters of dehydrated castor oil,<sup>66</sup> and Riemenschneider, Swift, and Sando separated the fats of cottonseed<sup>67</sup> oil. The constitution of lignin was investigated by Bailey,<sup>68</sup> who also made contributions to still design. Baxter and Robeson have used the



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## MOLECULAR REARRANGEMENTS

include isomeric changes (v. ISOMERISM, Vol. VII, 67a) and also reactions involving the structural or stereochemical rearrangements characteristic of isomeric change accompanied by decomposition, such as dehydration, or other further reaction. Certain particular isomeric changes are treated under separate titles, e.g., stereochemistry and tautomerism.

## Classification.

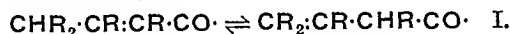
Molecular rearrangements have been classified in various ways but there is no comprehensive scheme and different relationships are emphasised by different authorities. Classification can be based on the structural changes involved, e.g., migrations of atoms or groups from carbon to carbon, or from nitrogen to carbon, or from side-chains in aromatic compounds into the nucleus. This classification is often convenient but it should be noted that in many cases the transfer of a radical from, e.g., nitrogen to carbon is accompanied by the converse transfer of another atom or group, commonly hydrogen. In some cases theoretical significance can be given to this classification by using it to draw attention to the nature of the bonds broken and formed in the reactions.

Lapworth (J.C.S. 1898, 73, 445) drew attention to the frequent occurrence of "αy-changes" in systems of the type



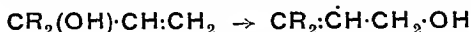


addition of proton to the  $\alpha$ - or  $\gamma$ - position in this ion forms the two isomers and in this way the reversible prototropic change is effected (*cf.* tautomerism).

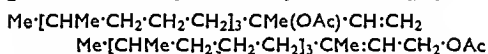


The corresponding anionotropic changes, which are useful in synthesis and also theoretically interesting, most commonly occur in

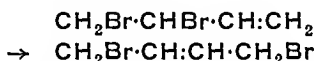
"allyloid systems,"  $\cdot \dot{\text{C}} : \dot{\text{C}} : \dot{\text{C}} \cdot \text{Y}$  in which Y is readily removed with both its bonding electrons (Allan, Oxford, Robinson, and Smith, J.C.S. 1926, 404; Whitmore, *l.c.*). The rearrangement



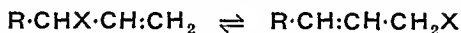
takes place either directly under the influence of acid or through esters or halides. The conversion of tertiary to primary alcohol predominates and this is one of the most useful reactions of this type for synthesis, *e.g.*, the penultimate stage of the synthesis of phytol:



The conversion of butadiene 1:2-dibromide into the 1:4-dibromide in presence of hydrogen bromide has an important significance in the study of 1:4-addition (Gillet, Bull. Soc. chim. Belg. 1922, 31, 366; Farmer and Scott, J.C.S. 1929, 172).



The interconversion of  $\alpha$ -phenylallyl and cinnamyl alcohols and their derivatives has been very fully investigated and discussed by Burton and Ingold (*ibid.* 1928, 904, 1650; 1929, 455). These rearrangements are of the general form:



where R = a hydrocarbon radical, generally phenyl or substituted phenyl;

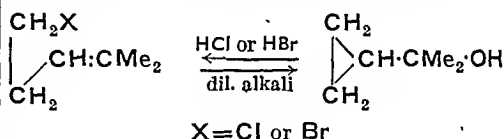
X =  $-\text{OH}$  or an ester or halogen group.

The ease with which X separates as an anion will depend (1) on the ionic stability of X' as indicated, for example, by the strength of the acid HX; (2) on the stability of the carbonium ion, which is most commonly raised by resonance involving the group R; and (3) on the presence of cations in the reaction mixture or on the dielectric constant of the solvent.  $\alpha$ -Phenylallyl and cinnamyl alcohols can be isolated and esterified without change of structure. The esters (*e.g.*, acetate and *p*-nitrobenzoate) undergo interconversion in non-hydroxylic solvents, as do the alcohols in presence of strong acids, the cinnamyl being the more stable and predominant isomer. The bromides are so mobile that only the cinnamyl can be isolated. This sequence of mobility clearly follows factor (1) above.

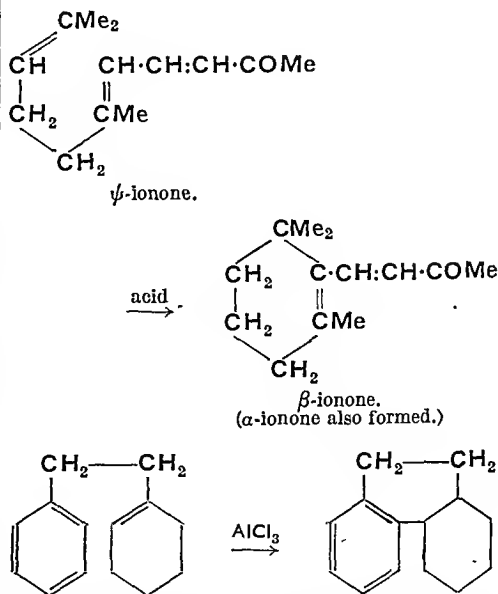
Comparisons of the influence of substituents in systems of the type  $\text{R} \cdot \text{CHX} \cdot \text{CH} : \text{CHR}$  showed that in facilitating the conversion and displacing the equilibrium the effectiveness of groups diminishes in the sequence  $p\text{-ClC}_6\text{H}_4$ ,

$p\text{-MeC}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , Me, H, in accordance with (2) above. Burton and Ingold also confirmed their generalisation (3) by showing that the ease of the  $\alpha$ -phenylallyl-cinnamyl conversion in different solvents diminished in the sequence benzonitrile, acetic anhydride, chlorobenzene, *p*-xylene (dielectric constants 26, 21, 6, 2 respectively) and similar reactions have also been found to take place most readily in ionising solvents. The conversion of  $\alpha$ -phenylallyl *p*-nitrobenzoate in presence of tetramethylammonium acetate gave a considerable amount of cinnamyl acetate, showing that the change is not intramolecular but involves the anions in solution (*cf.* Meisenheimer and Beutter, Annalen, 1934, 508, 58).

Cyclisation of polyenes and of aromatic compounds with unsaturated side-chains is usually brought about by the action of acids or aluminium chloride, and constitutes an important type of isomeric change. An unusual type of reversible cyclisation is closely related to the anionotropic changes just discussed:



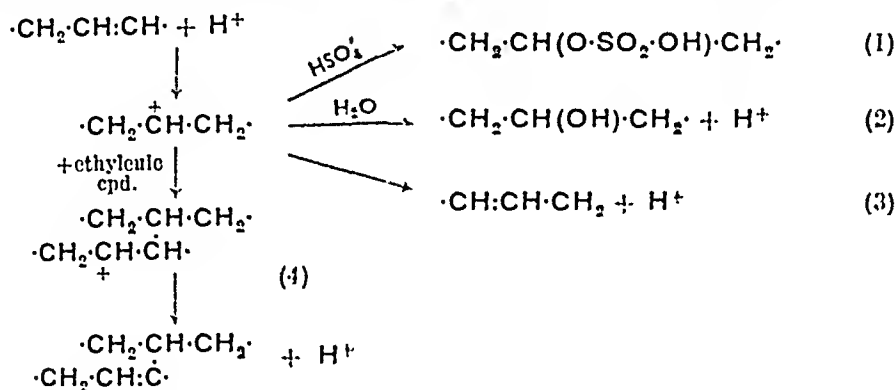
(Bruylants and Dewael, Bull. Acad. roy. Belg. 1928, [v], 14, 140). The great numbers of more typical cyclisations (*cf.* L. F. Fieser, "The Chemistry of Natural Products Related to Phenanthrene," New York, Reinhold Pub. Corp. 1937) can be illustrated by one example involving a polyene structure with acid and another involving an aromatic compound with aluminium chloride. In both cases six membered rings are formed but the formation of five membered rings is also fairly common.



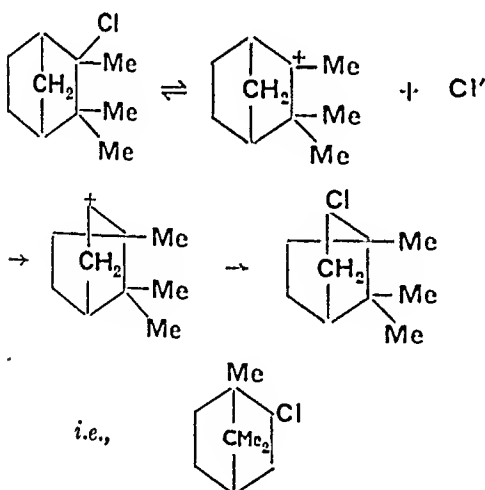
The mechanism of the cyclisation of polyenes by acid is considered to be related to other

reactions of ethylenic compounds. When an ethylenic bond reacts with a strong acid, a proton first adds to one of the carbon atoms forming a positivo (carbonium) ion similar to those formed by the removal of a negative ion from a halide or alcohol as in the anionotropic changes discussed above. This ion can (1) take up a negative ion, *e.g.*, complete the addition of the acid, (2) take up a hydroxylic solvent and lose proton

from it giving, for example, hydration, (3) lose proton from a different part of the molecule forming an isomeric ethylenic compound as in the movement of double bonds considered above, (4) combine with another unsaturated centre and if this is in another part of the same molecule, by subsequent loss of another proton complete the cyclisation, or if it is in another similar molecule give polymerisation:



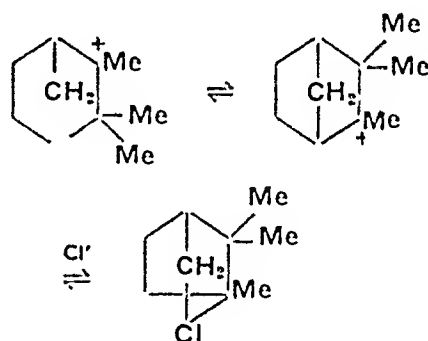
Wagner-Meerwein rearrangements occur with *monohydric alcohols* and their derivatives. They are initiated in circumstances similar to many of the above reactions but involve the breaking of single bonds between carbon atoms leading to different arrangements of carbon skeletons in ring systems or open chains. A number of typical examples are found in the terpene series, *e.g.*, the conversion of camphene hydrochloride to isobornyl chloride which has been carefully studied. The carbonium ion, mechanism (Meerwein and Wortmann, *Annalen*, 1924, 435, 190; *cf.* Meerwein and Van Emster, *Ber.* 1922, 55 [B], 2500; Whitmore, *l.c.*) is:



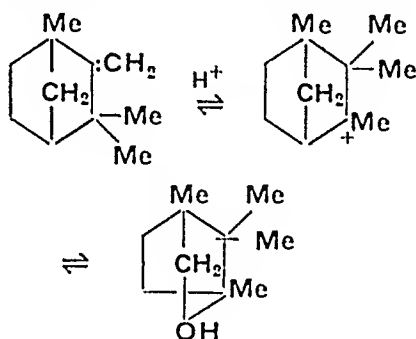
This reaction is practically instantaneous in cresol and in sulphur dioxide, in which triphenylmethyl chloride is extensively ionised. It is generally accelerated by solvents and reagents and in derivatives which favour ionisation, *e.g.*, in chlorobenzene it is accelerated by halides which have an affinity for chlorine ions such as stannic chloride, in nitrobenzene by hydrogen chloride but not markedly so by lithium chloride, and the rearrangement of analogous camphene derivatives gives the se-

quence of diminishing rates as bromide, chlorocymolsulphonate, chloride, chloroacetate (Hammett, *op. cit.*, p. 319). These rearrangements may involve dehydration (borneol to camphene) and are reversible.

The first of the two carbonium ions represented above can undergo an alternative Wagner-Meerwein change by the migration of a methyl group to give an ion identical in structure but not in stereochemical configuration to itself, and this will also give isobornyl chloride by ring change and addition of halide ion:

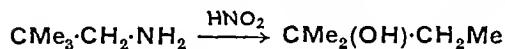
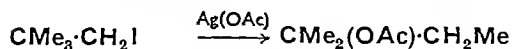
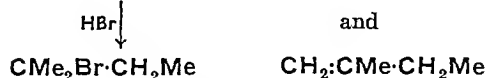
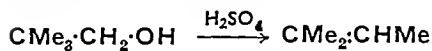


Nametkin and collaborators (*Annalen*, 1927, 459, 144; *cf.* *J. pr. Chem.* 1932, [ii], 135, 155) showed that  $\alpha$ -methylcamphene gives 4-methylisoborneol, and not the 6-isomer, clearly by an analogous series of rearrangements:



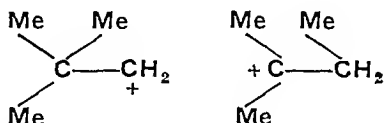
Houben and Pfankuch (Annalen, 1931, 489, 193) have pointed out that the stereochemical changes in the camphene-isobornyl chloride and similar rearrangements are accounted for by a similar mechanism, so that the more complex mechanism also applies in these cases (Chem. Soc. Annual Rep. 1932, 29, 147).

Wagner-Meerwein changes have also been investigated in less complex molecules such as neopentyl derivatives (Freund and Lenze, Ber. 1891, 24, 2150; Whitmore and Fleming, J.C.S. 1934, 1269). These may be summarised as follows:

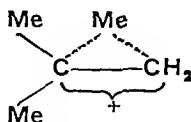


In all these cases the reagents are such as would tend to the removal of  $-\text{OH}$ , halogen, or  $-\text{NH}_2$  leaving a positive carbonium ion.

Thus the evidence for the formation of free carbonium ions is stronger in these various examples of the Wagner-Meerwein changes than in most other cases but the rearrangement of C-C linkages is clearly intramolecular and most probably arises from the resonance possibilities in the ion, as suggested by Ingold (Chem. Soc. Annual Rep. 1939, 36, 197). Canonical states are



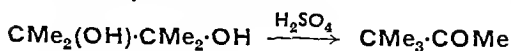
or together



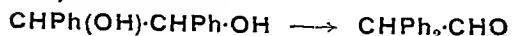
This explanation is applicable to many different migrations of hydrocarbon groups whether the free carbonium ion is formed or not. In the main it is the quantum theory equivalent of Robinson's partial valency system (Mem. Manchester Phil. Soc. 1920, 64, 7) and its first electronic equivalent.

Glycols and related compounds undergo reactions which are very similar to Wagner-Meerwein changes. They may be classified in terms of examples as follows:

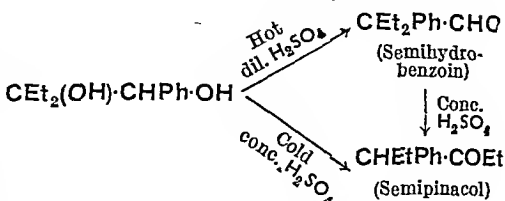
Pinacol-pinacolone.—



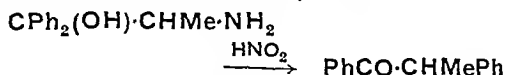
Hydrobenzoin.—



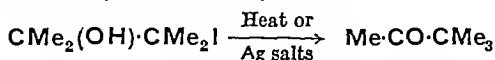
Semipinacol and Semihydrobenzoin.—



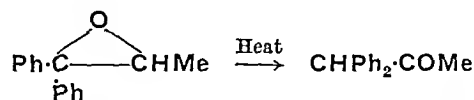
Aminoalcohol Decomposition.—



Iodohydrin Decomposition.—



Ethylene Oxide Rearrangement.—



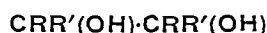
These reactions have been very fully investigated and discussed over a long period (Chem. Soc. Annual Rep. 1924, 21, 96; 1925, 22, 115; 1928, 25, 124; 1930, 27, 114; 1933, 30, 181; 1939, 36, 195. E. S. Wallis, *op. cit.*, gives a particularly full discussion and various aspects are considered in the works referred to above). The conditions and mechanisms are exactly parallel to those indicated for the Wagner-Meerwein changes above but more complex considerations govern the migrations about which much information is available. The generalisations cover most of this but are still not fully comprehensive.

The starting materials can all be expressed by the general formula



where R is a hydrocarbon group or hydrogen and X and Y electronegative elements or in the oxides a divalent oxygen. The primary factor in determining which group shall migrate is the tendency of X or Y to separate as a negative ion. In the halogenohydrin and aminoalcohol reactions the halogen or amino-group is removed with the bonding electrons and a group from the other central carbon atom migrates to take its place. Where X and Y are both OH the effect of the groups R in facilitating the loss of hydroxyl ion dominates the reaction and the order in which pairs of groups R act in this way is, for example, alkyl, alkyl > phenyl, H; or  $\alpha$ -naphthyl, H > benzyl, benzyl; or alkyl, benzyl > methyl, H. A similar sequence applies to the opening of the ethylene oxide ring and this generally determines the product in that isomerisation.

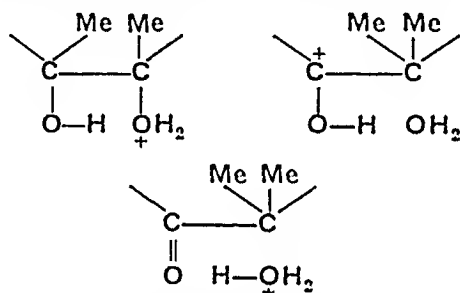
In the generalised system



the molecule is symmetrical and neither of the two factors so far considered will determine the

product obtained, but a sequence has been evolved for the "migratory aptitudes" of groups which may be approximated to: *p*-anisyl > *p*-tolyl, *p*-diphenyl > *α*-naphthyl > *p*-isopropylphenyl > *p*-ethylphenyl, *p*-fluorophenyl, phenyl > *p*-iodophenyl > *p*-chlorophenyl, *m*-tolyl, *m*-anisyl > *m*-chlorophenyl. In general, high electron availability at the point of attachment to the glycol carbon facilitates migration, in accord with the transfer of the group to a positive carbon, but there are individual exceptions.

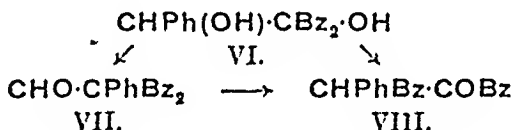
Stereochemical observations have thrown light on the detail of these arrangements. For example, when *cis*- and *trans*-1:2-dimethylcyclopentane-1:2-diols are refluxed with 30% sulphuric acid, the *cis*-form undergoes the pinacol-pinacolone change to 2:2-dimethylcyclopentanone (87% yield) but the *trans*-isomer gives tar (Bartlett and Pöckel, J. Amer. Chem. Soc. 1937, 59, 820; Bartlett and Bayley, *ibid.* 1938, 60, 2416). These results indicate an inversion reaction and this suggests that rearrangement accompanies ionisation rather than taking place in the free positive ion. The addition of proton to the glycol gives a positive ion which can be represented by the following canonical states:



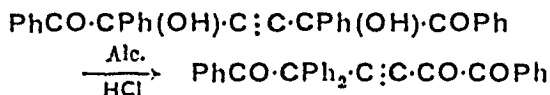
The solvent has an important influence on the completion of the reaction and should be in-

cluded in a fuller consideration of the reaction mechanism.

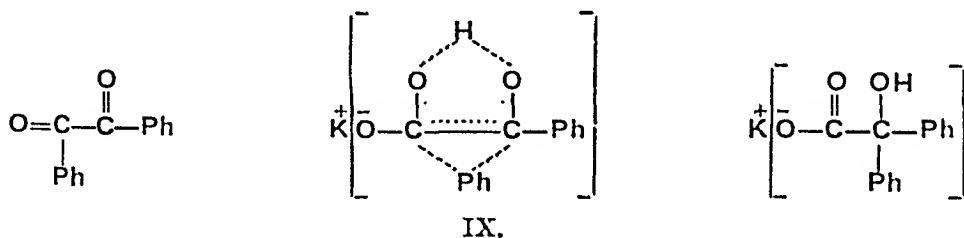
In a number of other cases incomplete racemisation during rearrangement supports a mechanism of the above type rather than prior ionisation. Similarly since Roger and Mackenzie (Ber. 1929, 62 [B], 272) showed that VI is converted into VIII without complete racemisation, it has been clear that the inactive aldehyde VII is not the main intermediate as had been suggested, although aldehydes of the type VII can also be converted to ketones of the type VIII by acids.



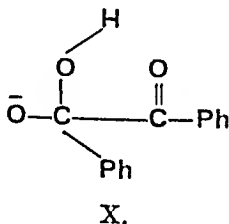
The following example indicates that with suitable structures *αδ*-migrations of the pinacol type can take place (Kleinfeller and Eckert, *ibid.* 1929, 62 [B], 1598; cf. E. R. H. Jones, Chem. Soc. Annual Rep. 1914, 41, 169, 175):



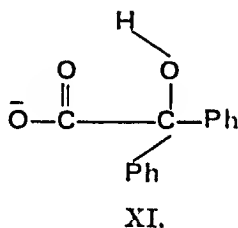
The Benzilic Acid change differs from the other carbon to carbon migrations considered above in that it is carried out in alkaline solution, and indeed the reaction takes place through the negative ion formed by the addition of hydroxyl ion to benzil. Robinson's mechanism (Chem. Soc. Annual Rep. 1923, 20, 118) (IX) translates directly into resonance terms (canonical states X and XI). It is not clear that the hydrogen



IX.



X.



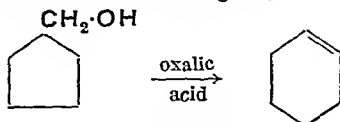
XI.

migrates from one oxygen to another in the same process as the phenyl moves from carbon to carbon but this is not improbable. The resemblance to the mechanisms of the Wagner-Meerwein and pinacol rearrangements is clear, but in this case the presence of the negatively charged oxygen is to be regarded as the main driving force leading to the transfer of phenyl

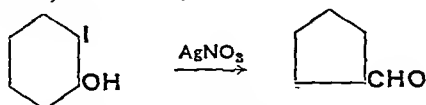
to the adjacent electron-accepting carbonyl carbon.

Many of the preparative and synthetic uses of these changes of the Wagner-Meerwein, pinacol, and benzilic acid types are obvious from this outline. Their application to alicyclic compounds leads to a variety of changes in ring structure, which have been indicated for the first

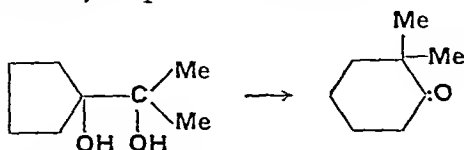
type and which can be applied for the enlargement and diminution of rings, *e.g.*,



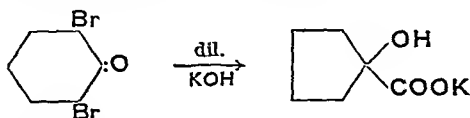
Rosanov, J.C.S. 1915, 108, 657.



Tiffeneau, Compt. rend. 1914, 159, 771.



Meerwein, Annalen, 1910, 376, 152.

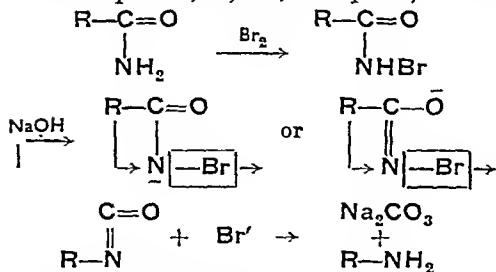


Wallach, J.C.S. 1916, 110, 487.

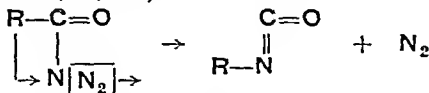
#### B. MIGRATIONS FROM CARBON TO NITROGEN, NITROGEN TO CARBON, OXYGEN TO CARBON, ETC.

Four types of rearrangement under this general heading are fairly closely related to the Wagner-Meerwein changes and to one another. This is indicated in the following scheme:

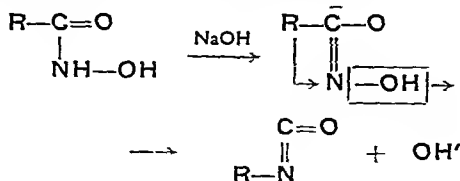
Hofmann Degradation of Amides (Hofmann, Ber. 1882, 15, 407; Watson, Chem. Soc. Annual Rep. 1939, 36, 193, and *op. cit.*).—



Curtius Decomposition of Azides (Curtius, Ber. 1894, 27, 778).—

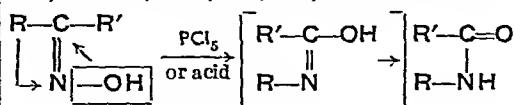


Lossen Decomposition of Hydroxamic Acids (Lossen, Annalen, 1869, 150, 314; 1894, 281, 169).—

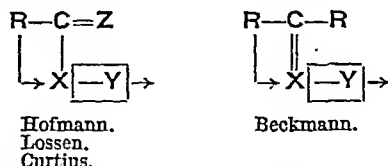


The formula given for the negative hydroxamic ion is not the normal one, but emphasises the relationship to the other rearrangements and is one canonical state of a probable intermediate.

Beckmann Rearrangement of Oximes (Beckmann, Ber. 1886, 19, 988; Blatt, Chemical Reviews, 1933, 12, 215; B. Jones, *ibid.* 1944, 35, 335; Nature, 1946, 157, 519).—



The first three reactions occur in alkaline solution, but in some cases it has been shown that the rate is only slightly dependent on the concentration of alkali (Van Dam and Arberson, Rec. trav. chim. 1900, 19, 318). The Beckmann rearrangement is carried out in acids or in neutral ionising media. All these reactions can be generalised as



The reactions are facilitated by high stability of Y as a negative ion (*e.g.*, in the series  $\text{Br} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{A}$ ) and by electron repulsive effects in R (*e.g.*, in various groups  $\cdot \text{C}_6\text{H}_4\text{A}$ ) and in X (Hauser and Renfrow, J. Amer. Chem. Soc. 1937, 59, 121; Bright and Hauser, *ibid.* 1939, 61, 618), in accordance with the view that separation of Y with its bonding electrons and the subsequent or simultaneous transfer of R with its bonding electrons are the key factors in the mechanism of these reactions (*cf.* Wagner-Meerwein and pinacol transformations). It is clear that the migration of R is intramolecular. The best evidence is stereochemical (E. S. Wallis *et al.*, *ibid.* 1926–1933). Racemisation does not occur in the rearrangement of derivatives of benzylmethylacetic acid



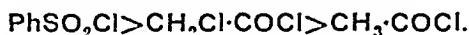
and the rotations of the amines or ureas obtained from amide, azide, or hydroxamate are identical. Only one isocyanate is obtained when benzylmethylacetazide is degraded in presence of triphenylmethyl radicals, indicating that R does not separate as a free radical. In *d*-3:5-dinitro-6- $\alpha$ -naphthylbenzamide optical activity arises from restricted rotation in the bond joining the benzene and naphthalene nuclei and this activity is completely preserved during the Hofmann degradation, whereas dissociation at any stage would have permitted free rotation and racemisation.

The Beckmann rearrangement of oximes requires further discussion. It was first carried out by the action of phosphorus pentachloride and subsequently was found to be caused also by phosphorus pentoxide, concentrated sulphuric acid, hydrogen chloride, and also by converting the oximes to esters ( $\text{:N}\cdot\text{OX}$ ), especially those of strong acids. The isomerisation takes place either during the ester formation or on heating the esters alone or in a

solvent. Ketoximes generally undergo the Beckmann rearrangement smoothly; some aldioximes and their N-ethers also do so.

This rearrangement has been much used for the establishment of the stereochemical configuration of the isomeric oximes, as suggested by Hantzsch and Werner (Ber. 1890, 23, 11; 1891, 24, 13, 51). The two stereoisomers of most of the ketoximes gave different single amides and for a long time it was considered that the OH changed places with the adjacent group R. Meisenheimer (*ibid.* 1921, 54, 3206; Annalen, 1925, 446, 205) showed from other evidence that it is the opposite group R' which migrates, as represented on p. 180c and this evidence has been supplemented by other workers (Chem. Soc. Annual Rep. 1925, 22, 105; 1926, 23, 126).

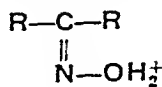
The mechanism of the Beckmann rearrangement has been the subject of a long sequence of investigations. The action of phosphorus pentachloride and hydrogen chloride led to the suggestion that with these reagents the chloroimino derivative ( $\text{CR}_2\text{:NCl}$ ) is an intermediate, but Stieglitz and Peterson showed that such derivatives are not labile in this way (Ber. 1910, 43, 782; cf. Amer. Chem. J. 1911, 46, 325). This remains a surprising observation in relation to further work. M. Kuhara ("On the Beckmann Rearrangement," Imperial University of Tokio, 1926) showed that the speed of rearrangement of benzophenone oxime was influenced by acid chlorides in the order



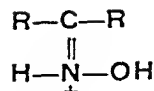
He isolated the benzenesulphonyl ester and showed that at its m.p., 62°, the pure ester rearranges to a sulphonyl derivative which gives benzanilide on hydrolysis, whereas the acetate or free oxime requires an acid catalyst to cause the conversion (cf. Kuhara, Agatsuma and Araki, Mem. Coll. Sci. Kyoto, 1917, 3, 1).

Chapman and his collaborators (J.C.S. 1933-1936) showed that oxime picrates also undergo rearrangement by heating alone, whereas the 2:4-dinitrophenates do not. This suggests a rather sharp threshold strength of acid for the conversion of the corresponding ester. The rearrangement of the picrate is accelerated in solvents of high dielectric constant, e.g., it is 35 times as fast in ethylene dichloride as in benzene, and the addition of polar solvents to solutions in carbon tetrachloride gives rates in the order of the dielectric constants, viz. hexane < chlorobenzene < ethylene dichloride < acetone < nitrobenzene < acetonitrile. In non-polar solvents the order of the reaction is greater than unity, since the polar character of the oxime picrate and the products has a catalytic effect.

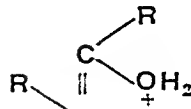
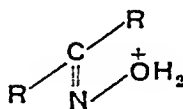
The trend of all this evidence suggests a mechanism analogous to that of the Wagner-Meerwein and related changes (cf. p. 177a). The highly specific stereochemical features of this rearrangement suggest that both parts of the change are intramolecular. Strong acids presumably catalyse the change of oximes and their esters through the formation of positive ions of the form XII rather than through the normal salt ion XIII.



XII.

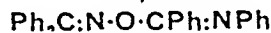
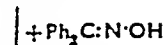
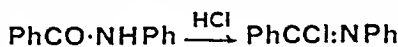


XIII.



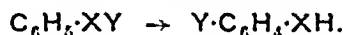
XIV.

Chapman also made a study of the rearrangement of benzophenone oxime in ethylene dichloride in presence of hydrogen chloride and showed that the direct conversion was only a major reaction during the marked induction period, after which the reaction proceeded at a much greater and nearly constant speed through the following reactions:

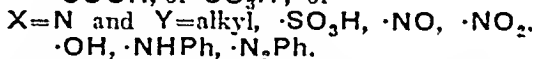
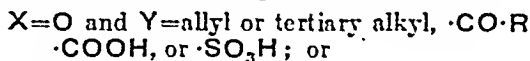


This last cation resembles the ester of a strong acid and undergoes rapid rearrangement. It is not yet clear to what extent similar ester formations are important in Beckmann rearrangements under other conditions.

#### MIGRATIONS FROM SIDE-CHAINS INTO AROMATIC NUCLEI.



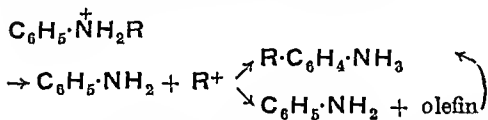
A variety of rearrangements under this general heading can be represented by the above formulae where for example



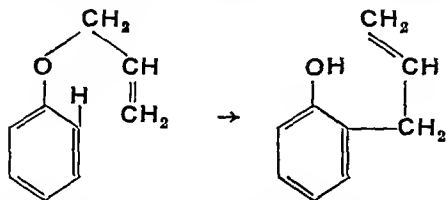
*Migration of Hydrocarbon Groups and Derivatives.*—Hofmann and Martius (Ber. 1871, 4, 742; cf. *ibid.* 1885, 18, 1821) observed that nuclear alkylation of aniline, as well as side-chain alkylation, occurred when aniline hydrochloride is heated under pressure with methyl alcohol. Dimethyltoluidine and dimethylxyldene were amongst the products. Hofmann further showed that when trimethylphenylammonium iodide is heated under pressure the methyl groups migrate into the nucleus, until, at 335°, the main product is mesidine (2:4:6-trimethylaniline). The alkyl groups here enter the *o*- and *p*-positions, but Hey and his co-workers, continuing the study of nuclear alkylation of the hydrochlorides of *o*- and *p*-toluidine, mesidine and dimethylmesidine in methyl alcohol, found amongst the products isodurindine in which methyl has entered the *m*-position after completion of *o-p*-alkylation. They also identified hydrocarbons (including

hexamethylbenzene), phenols and alkylated acridine derivatives (J.C.S. 1927-1937).

The free alkylanilines do not undergo rearrangement by the action of heat alone, but Reilly and Hickinbottom (*ibid.* 1920, 117, 103) showed that these reactions also occur on heating alkylanilines with metallic chlorides such as those of cobalt, cadmium, or magnesium. Hickinbottom's further studies of these reactions have thrown light on their mechanism (*ibid.* 1927-1937). Ethylaniline was heated with cobalt chloride at 240-270° in a vertical glass tube designed for the collection of volatile products from time to time. No ethyl chloride was obtained and the yield of aniline was negligible. A similar result was obtained with *n*-butylaniline but *isobutyl*- and *tert.*-butylaniline gave good yields of the butylenes, whereas under conditions precluding the escape of butylenes rearrangement was observed. Hickinbottom concludes that the mechanism is primarily a dissociation giving positive alkyl ions which re-alkylate in the nucleus or decompose into proton and olefin, which under appropriate conditions can also act as an alkylating agent. The acid-catalysed rearrangement can be represented as :



Phenyl ethers (especially allyl, benzyl, triphenylmethyl and *tert.*-alkyl ethers of phenols) undergo isomerisations analogous to the Hofmann-Martius reaction.  $\beta$ -Naphthyl allyl ether is completely converted to 1-allyl-2-naphthol at 210°. On the other hand phenyl benzyl ether is only partly converted into 4-hydroxydiphenylmethane by heating with zinc chloride at 160°. With aluminium chloride other groups can be made to migrate from oxygen to the nucleus and also migrate from one position in the nucleus to another (see Baddeley, *ibid.* 1943, 273). Claisen considered that the *o*-migration of allyl groups involved the attachment of the  $\gamma$ -allyl carbon to the *o*-position :

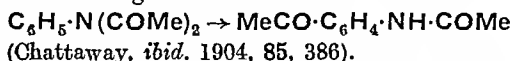


Phenyl cinnamyl and  $\beta$ -naphthyl allyl ethers heated together rearrange quite independently (Hurd and Smerling, J. Amer. Chem. Soc. 1937, 59, 107) and the intramolecular nature of the reaction seems clear. With alkyl groups, other than the special allyl case, migration of positive alkyl ions seems the probable mechanism. Olefin is formed when the *o*-*p*-positions are blocked.

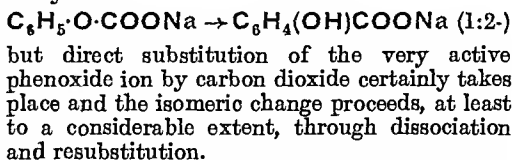
The very similar *Fries rearrangement* (Fries and collaborators, Ber. 1908, 41, 4272; von Auwers, Annalen, 1926, 447, 162; 1928, 460, 240; Cox, J. Amer. Chem. Soc. 1930, 52, 352;

W. Baker, J.C.S. 1934, 1684) is carried out by heating phenyl esters of carboxylic acids with aluminium, zinc, or ferric chlorides, when the acyl group migrates to the *o*-position and less easily to the *p*-position. When these reactions are carried out in diphenyl ether the acyl group enters the solvent, and in presence of alcohols esters are formed. Hence the acyl group is separated in these reactions and the mechanism is at least partly intermolecular.

Acetanilide does not undergo a similar reaction but the diacetyl derivative readily does so on heating with zinc chloride :



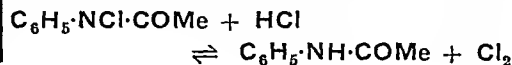
The *Kolbe synthesis* of salicylic acid (Annalen, 1860, 113, 126; J. pr. Chem. 1875, [ii], 11, 24; Schmitt, *ibid.* 1885, [ii], 31, 397; Tijinstra, Ber. 1905, 38, 1375) may partly involve the conversion of sodium phenyl carbonate to sodium salicylate :



*Migration of Sulphonic, Nitro, and Nitroso Groups.*—Most of the substitution reactions of aromatic amines and a few of those of phenols involve initial attack on the side-chain followed by a rearrangement to the nuclear substituted product. Phenylsulphuric acids and their salts (Baumann, *ibid.* 1878, 11, 1910; Van Charante, Rec. trav. chim. 1908, 27, 59), arylsulphamic acids and their salts on heating alone, and sulphanimides (e.g.  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{SO}_2\text{Ph}$ ) on heating with 80% sulphuric acid undergo changes leading to the formation of, e.g., phenol-*p*-sulphonic acid, aniline-*o*-sulphonic acid and -*p*-sulphonic acid, and in the sulphonamide example 2-ethylamino-5-methyldiphenylsulphone. The mechanism appears to be fission and resubstitution.

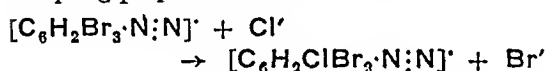
Aromatic amines with nitric acid in acetic anhydride give *nitroamines* which are converted by acids to *o*- and *p*-nitroanilines (Orton, Brit. Assoc. Rep. 1912, 117; Bradfield and Orton, J.C.S. 1929, 915). The reaction appears to be intramolecular, in contrast to the reaction of aromatic nitrosamines with hydrogen chloride to give nitrosoanilines together with chlorinated amines, clearly by a reaction involving the formation of nitrosyl chloride or oxides of nitrogen and chlorine (Fischer and Hipp, Ber. 1887, 20, 1247; cf. *ibid.* 1912, 45, 1098).

*Migration of Halogen.*—*N*-Chloroacetanilide is isolated by the action of hypochlorous acid on acetanilide. Its conversion to *o*- and *p*-chloroacetanilides is also in marked contrast to the nitroamine change and is one of the clearest cases of intermolecular rearrangement. Orton and his collaborators (Brit. Assoc. Rep. 1910, 85; J.C.S. 1928, 998; Olsen and Hornel, J. Org. Chem. 1938, 3, 76) showed that hydrogen chloride is a specific catalyst and the equilibrium



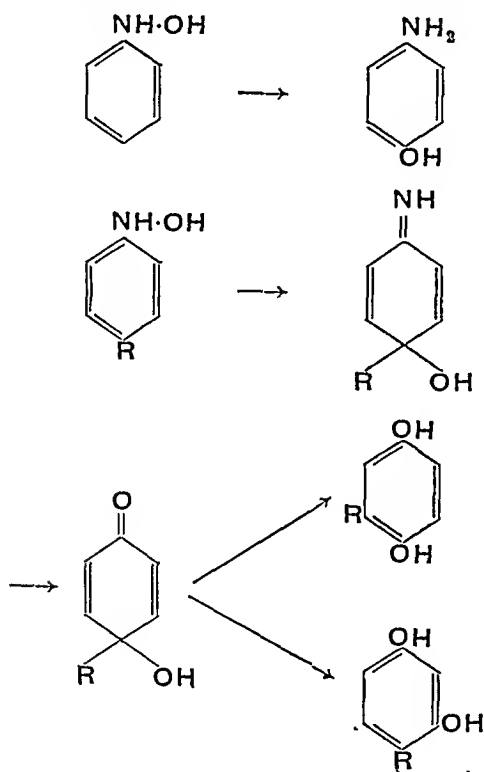
is established. The free chlorine irreversibly chlorinates the aromatic nucleus in acetanilide giving *p*-chloroacetanilide with some *o*-isomer. Phenols, amines, and other anilides present in the system, if sufficiently active, are also chlorinated. In contrast to this behaviour in aqueous solutions, the rearrangement of *N*-halogenated anilides in non-hydroxylic solvents is an intramolecular process catalysed by acids generally with no specific effect from hydrogen chloride (Bell *et al.*, Proc. Roy. Soc. 1934, A, 143, 377; J.C.S. 1939, 1096, 1774).

2:4:6-tribromobenzenediazonium chloride is converted, by heating in alcohol-ether solution, into 4-chloro-2:6-dibromobenzenediazonium bromide (Hantsch and Smyth, Ber. 1900, 33, 505; cf. studies by Hantsch and collaborators on other similar reactions). The free halogen ion displaces the halogen in the *p*-position relative to the positive pole. The factors operating resemble those which lead to replacement of halogen in *o*- and *p*-chloronitrobenzenes in which the reactive positions show electron accepting properties. This reaction is



and is included here as a case of migration of halogen from side-chain to nucleus but in mechanism it in no way resembles the other examples above.

*Migration of Hydroxyl and Related Groups.*—*Arylhydroxylamines* heated with sulphuric acid undergo, amongst other reactions, rearrangement to give *p*-aminophenols, if the *p*-position is free and, if it is not free, iminoquinol, hydroquinone, and resorcinol derivatives (Gattermann, *ibid.* 1893, 26, 1844; Bamberger, *ibid.* 1907, 40, 1893). The reactions can be represented as:



Azoxybenzene heated with sulphuric acid undergoes a somewhat similar rearrangement (Wallach and Billi, Ber. 1880, 13, 525; Lachman, J. Amer. Chem. Soc. 1902, 24, 1178):

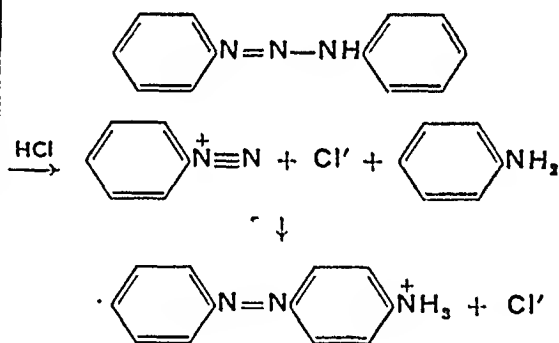


Tertiary aromatic amino oxides saturated with sulphur dioxide also give the corresponding alkylaminophenols (Bamberger and Tschirner, Ber. 1899, 32, 1882).

*Migration of Amino Groups and Derivatives.*—The partial conversion of phenylhydrazine hydrochloride to the hydrochloride of *p*-phenylenediamine by heating at 200° bears at least a formal relationship to several of the other migrations from side-chains discussed above and also to the benzidine change.

The two reactions under this general heading which have been most fully studied are the conversion of diazoaminobenzene to aminoazobenzene, a typical intermolecular reaction, and the benzidine change, one of the clearest cases of the intramolecular type.

Benzenediazonium salts couple with aniline in weakly acid solution to give diazoaminobenzene, which is converted to aminoazobenzene by heating with stronger acid. This reaction involves the following changes:

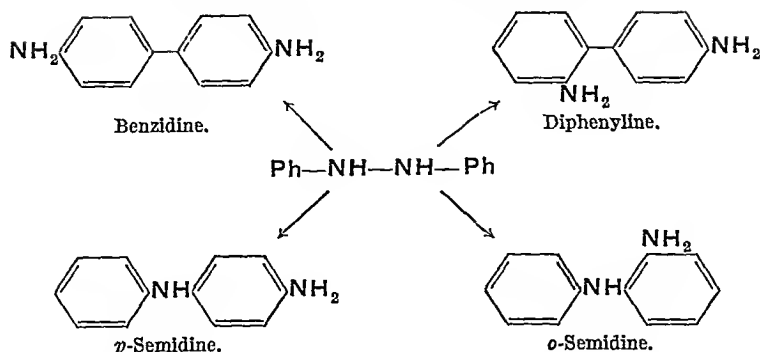


With some derivatives of the two reactants little or none of the diazoamino intermediate may be formed. When the *p*-position in the amine is occupied, the azo-coupling takes place in the *o*-position. If diazoaminotoluene is heated in solution with aniline hydrochloride the azo group enters the aniline, to give aminoazobenzene, and with  $\beta$ -naphthol in solution diazoaminobenzene gives a 90% yield of benzene-azo- $\beta$ -naphthol (Nietzki, *ibid.* 1877, 10, 662; Kidd, J. Org. Chem. 1937, 2, 198).

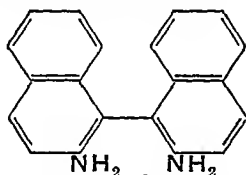
The conversion of hydrazobenzene (1:2-diphenylhydrazine) and its derivatives to benzidine and its derivatives or related compounds is one of the most important and interesting rearrangements and one of the most difficult fully to understand theoretically (Jacobsen, Annalen, 1922, 428, 76; Robinson, J.C.S. 1941, 220; Ingold, *ibid.* 1941, 608; see these summaries and discussions for further references). The following is a brief abstract from a great amount of information and discussion.

The four main types of product from these rearrangements can be represented as follows:





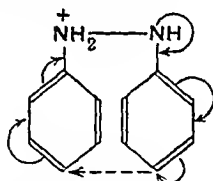
Hydrazobenzene and its derivatives generally give the corresponding benzidine as the main product if that is structurally possible and the yields are often very good. Substituents never exercise any directive power in the migration except in so far as they may occupy the *p*-position, thus preventing the formation of benzidines, so that one of the other possibilities, usually a semidine, becomes the main product. If the *p*-position is occupied by Cl, COOH, SO<sub>3</sub>H, or O·COME, this group is often eliminated and the benzidine formed. 3-Amino-diphenyl and o-benzidine (2:2'-diaminodiphenyl) derivatives are not formed, but 1:2-di- $\alpha$ -naphthylhydrazine gives both symmetrical diamines; 1:2-di- $\beta$ -naphthylhydrazine gives the o-benzidine type of product only:



An early and curiously persistent hypothesis postulated that *p*-semidine is an intermediate in the conversion of hydrazobenzene to benzidine, but Robinson and Robinson (1918) showed that the semidine is not converted to benzidine under the conditions of this reaction. The intramolecular character of the rearrangement is clearly shown by two types of evidence. Firstly, amongst the large number of examples of this rearrangement studied or reviewed by Jacobsen not one example was found in which A·NH·NH·B gave NH<sub>2</sub>·A·A·NH<sub>2</sub> or NH<sub>2</sub>·B·B·NH<sub>2</sub>; the product always contains both parts of the original molecule giving NH<sub>2</sub>·A·B·NH<sub>2</sub>. Secondly, when 2:2'-diethoxyhydrazobenzene and 2:2'-dimethoxyhydrazobenzene (dianisidine) were rearranged together, Ingold and Kidd showed by thermal analysis that methoxyethoxybenzidine is not formed but only diethoxy- and dimethoxybenzidines. With such closely related compounds any separation of the two parts would certainly have led to the production of the unsymmetrical product. This evidence appears sufficient, but it can be supported in various ways. For example, tetraphenylhydrazine (NPh<sub>2</sub>·NPh<sub>2</sub>) dissociates into free radicals and also undergoes the benzidine change but not under the conditions which favour dissociation.

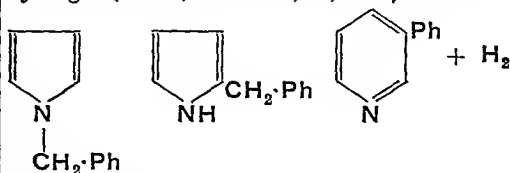
Robinson (*l.c.*) discusses the mechanism of the

reaction in terms of his electronic oscillation hypothesis applied to the positive ion of the hydrazobenzene salt, and Ingold (*l.c.*) gives an explanation in terms of resonance theory applied to the "formally neutral molecule." In spite of considerable differences, these explanations have a good deal in common and, particularly, both postulate the formation of new linkages before the complete fission of those between the nitrogens, and the facilitation of the formation of this transition state through the possibilities of electron redistribution which normally govern, for example, aromatic substitution. The following formula illustrates how the positive charge on one nitrogen in the ion of the salt leads in the normal way to a strongly electron accepting *p*-position in the attached benzene nucleus which will combine with the strongly donating position *p*- to the trivalent nitrogen in the other nucleus:



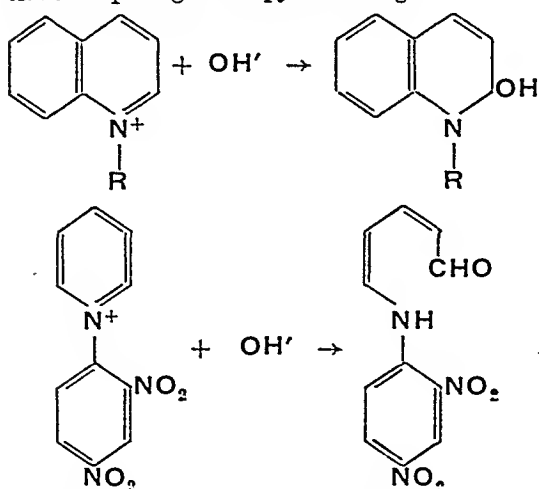
*Migrations in Heterocyclic Compounds.*—These are mainly migrations from the hetero-atom into the nucleus and can be illustrated by the following examples:

N-alkyl- and N-acyl-pyrroles give  $\alpha$ -alkyl and  $\alpha$ -acyl derivatives on heating (Ciamician and Zanetti, *Ber.* 1889, 22, 659, 2518), and the corresponding pyridine derivatives show migrations to both the  $\alpha$ - and the  $\gamma$ -positions (Lange, *ibid.* 1885, 18, 3436). N-benzylpyrrole undergoes one of the most interesting rearrangements in this type of compound, giving  $\alpha$ -benzylpyrrole and  $\beta$ -phenylpyridine. The formation of the latter product, presumably through the former, involves a ring enlargement and loss of hydrogen (Pictet, *ibid.* 1905, 38, 1946).



The conversion of the quaternary hydroxides of aromatic heterocyclic compounds to pseudo bases is formally an isomeric change, but it is essentially an addition reaction leading to at

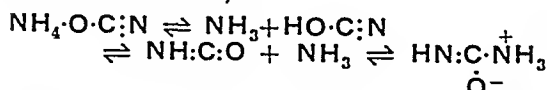
least partial loss of aromatic character. In N-(2,3-dinitrophenyl)-pyridines this reaction leads to opening of the pyridine ring.



In heterocyclic systems containing two or more hetero atoms, possibilities analogous to those indicated above arise and also some analogous to those included below under migrations between oxygen, nitrogen, and sulphur, etc.

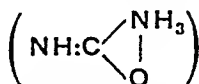
#### AMMONIUM CYANATE AND UREA.

The discovery of the change of ammonium cyanate into urea is recognised as a landmark in the history of chemistry because of its influence on the development of organic chemistry, as an example of the conversion of a compound obtained from typically mineral sources into so characteristic a product of metabolism (Wohler, *Annalen* (Poggendorf), 1828, 12, 253). The reaction is reversible and clearly involves dissociation into ammonia and cyanic acid (Chattaway, J.C.S. 1912, 101, 170) apparently giving the hydroxylic form of cyanic acid which isomerises to the keto form, the carbonyl group of which reacts with ammonia (E. A. Werner, *ibid.* 1913, 103, 1010; 1914, 105, 923; 1918, 111, 84 *et seq.*; "Chemistry of Urea," Longmans, Green and Co. 1923):



The kinetics of these reactions have been studied and discussed in detail (Werner, *op. cit.*),

in relation to the properties of urea and cyanic acid, and in particular to the cyclic formula for urea



a modern form of which is given above.

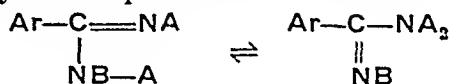
Ammonium thiocyanate gives thiourea on heating and hydrazine cyanate forms semi-carbazide.

#### C. MIGRATIONS BETWEEN OXYGEN, NITROGEN AND SULPHUR, ETC.

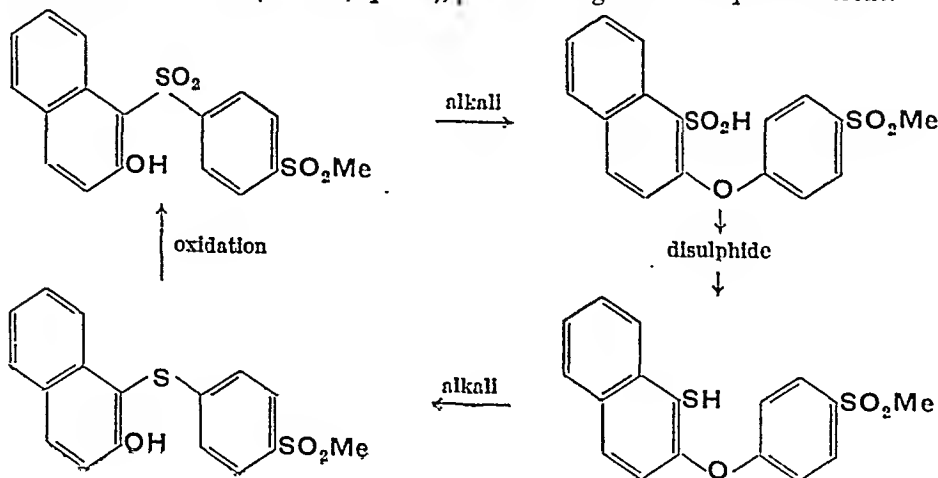
A great variety of miscellaneous reactions come under this heading. A number of them are reactions which commonly occur between reactive centres in different molecules and which become molecular rearrangements when the analogous reactive centres occur in the same molecule.

Raiford and collaborators studied very fully the migration of acyl groups in *o*-aminophenols (J. Amer. Chem. Soc. 1919-1925; cf. Nelson and Davis, *ibid.* 1926, 48, 1680).

One of the most extensively investigated groups of reactions under this general heading involves carboxylic and carbonic acid derivatives. Alkyl thiocyanates on heating give isothiocyanates (Johnson *et al.*, Amer. Chem. J. 1907-1908). Isocyanides give nitriles. Diaryl-thionearbonates,  $\text{CS}(\text{OAr})_2$ , give thioarbonates,  $\text{CO}(\text{OAr})\cdot\text{SAr}$  (von Vargha, Ber. 1930, 63 [B], 178). Imidols of the form  $\text{Ar}\cdot\text{C}(\text{OAr})\cdot\text{NAr}$  give amides  $\text{Ar}\cdot\text{CO}\cdot\text{NAr}_2$  and amidines undergo similar changes. Chapman and collaborators have made a detailed study of reactions of these last two types. Low electron availability in the migrating group facilitates both the forward and reverse reactions and high availability in the group B facilitates the reverse reaction. When two different amides or imidol ethers are mixed and rearranged they do so independently and no mixed product is formed. Thus the reactions are intramolecular. They can be represented as



The resemblance to the mechanism given for the Hofmann and related degradations is only superficial. The mechanisms and the factors determining them are quite different.





trum of a molecule, in contrast to its "electronic" spectrum. This explains the close association of infra-red with Raman spectra, for the latter also arise from changes in vibrational and rotational energy.

In 1928 it was discovered simultaneously by Landsberg and Mandelstam and by Raman that if a molecule is irradiated with visible or ultra-violet light of monochromatic frequency  $\nu$ , then the scattered light contains, in addition to the

original (or Rayleigh) frequency  $\nu$ , certain very much weaker companion frequencies  $\nu \pm \nu_1$ ,  $\nu \pm \nu_2 \dots$  where  $\nu_1$ ,  $\nu_2 \dots$  are of the same order of magnitude as vibrational and rotational frequencies occurring in the infra-red region of the spectrum, and in many cases are identical with observed infra-red absorption frequencies. The physical explanation of this is made clear in Fig. 2 from an energy level diagram for the molecule. Thus if  $E_0$  represents the state of

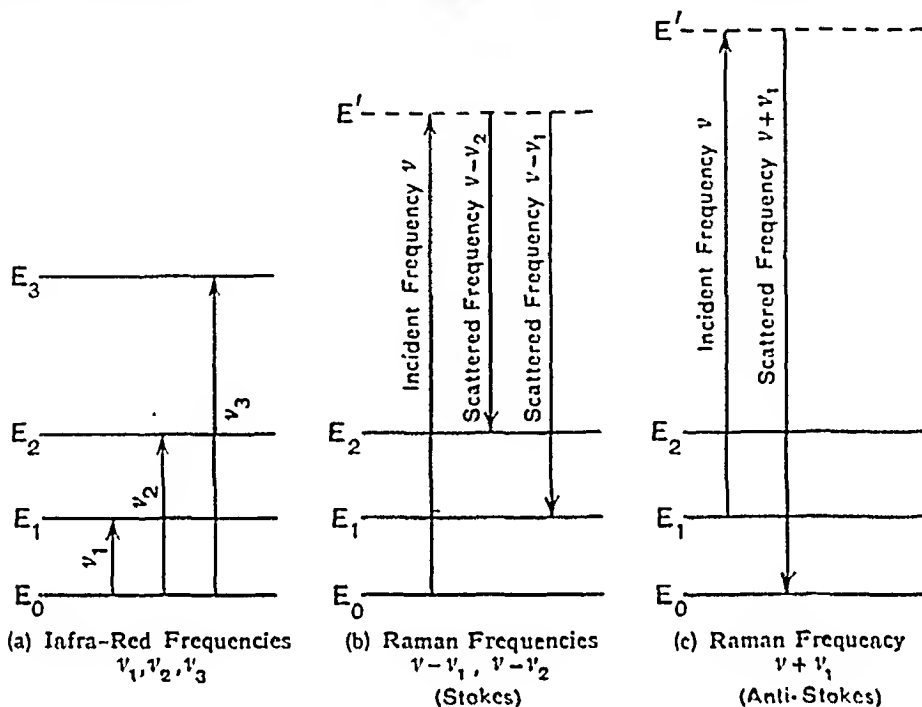


FIG. 2.

lowest energy, or "ground" state, of the molecule and  $E_1, E_2, E_3 \dots$  are vibrational energy levels corresponding to frequencies  $\nu_1, \nu_2, \nu_3 \dots$ , then absorption in the infra-red is due to a transition in which the molecule passes *directly* from  $E_0$  to  $E_1, E_2, E_3 \dots$ . The process of light scattering by a molecule is, however, to be pictured as an electronic absorption followed by an electronic emission. The incident frequency

$\nu$  is momentarily absorbed by the molecule, which is raised to some unstable electronic level  $E'$ , from which it immediately drops down either to the original state  $E_0$  or to some excited vibrational state  $E_1, E_2, E_3 \dots$ . In the former case the frequency of the scattered light is the same as that of the incident light, and this is known as *classical or Rayleigh scattering*; in the latter case the frequencies of the scattered light

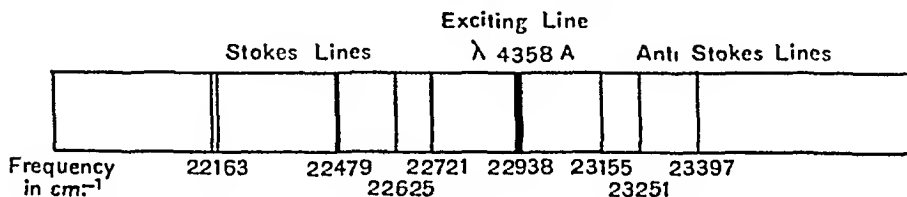


FIG. 3.

are less than that of the incident light, viz.  $\nu - \nu_1, \nu - \nu_2$ , etc.; this is known as *Raman scattering* and  $\nu_1, \nu_2$ , etc., are Raman frequencies of the molecule. It is clear that if light is incident on a molecule which is already in an excited state, and on scattering the molecule drops to the ground state, then the scattered frequency will be greater than the incident frequency, viz.  $\nu + \nu_1, \nu + \nu_2$ , etc. These cases of enhanced frequency are often referred to as

"*anti-Stokes frequencies*," in contrast to the cases of diminished frequency, which are known as "*Stokes frequencies*." Since the appearance of anti-Stokes frequencies depends on the occurrence of molecules in excited states, only the lower frequencies of a molecule ( $< 700 \text{ cm}^{-1}$ ) will appear as anti-Stokes frequencies in the Raman spectrum at ordinary temperatures. This is illustrated in Fig. 3, showing the Raman spectrum of carbon tetrachloride, in which the

frequencies 217, 313, 459, and 775  $\text{cm}^{-1}$  are excited as Stokes lines, but only 217, 313, and 459  $\text{cm}^{-1}$  as anti-Stokes lines. The foregoing discussion of Raman spectra has been limited to vibrational frequencies. Exactly similar arguments apply to the rotational frequencies, and rotational Raman spectra have been observed for some of the simpler polyatomic molecules. As it is necessary to have the molecules in the gaseous state in order to get rotational spectra and the intensity of the scattered light from gases is extremely weak and consequently hard to observe, pure rotational Raman spectra are not of great practical importance. For similar reasons the rotational fine structure which is superimposed on all vibrational Raman frequencies will be ignored in this article.

From a chemical standpoint infra-red and Raman spectra are important, not as a means of confirming the postulates of the quantum theory, but as tools for two main purposes, viz. (a) the determination of molecular structure, and (b) the identification of a particular compound in the presence of others from which it is hard to distinguish by chemical or other physical means. In the former case it is usually essential to have both the infra-red and the Raman spectrum of the molecule (in the gaseous state) under conditions of high resolving-power, and the complete interpretation of this spectrum requires a detailed knowledge of a specialised branch of quantum theory. In this article the

method of interpretation, indicating the limitations as well as the possibilities of this way of investigating molecular structure, is presented only in outline. The use of vibration spectra for purposes of identification naturally requires much less knowledge of the theory, and some general rules for interpretation can be given.

The present treatment is restricted to polyatomic molecules. The vibration spectra of diatomic molecules are of very little interest, since the information obtained from them can usually be obtained much more satisfactorily from electronic spectra (*v. this Vol., p. 197a et seq.*).

#### PRINCIPLES OF INTERPRETATION.

**Pure Rotation Spectra.**—The rotational energy of any molecule depends upon the moments of inertia of the molecule and upon certain quantum numbers controlling the quantisation of the angular momentum of the molecule. There are four possible cases, according to the degree of symmetry of the molecule. These are given in Table I, in which  $I_A$ ,  $I_B$ , and  $I_C$  are the three moments of inertia of the molecule,  $h$  is Planck's constant ( $6.56 \times 10^{-27}$  erg sec.<sup>-1</sup>), and  $J$  and  $K$  are rotational quantum numbers taking the values indicated. Pure rotation spectra arise from transitions between the rotational energy levels caused by emission, absorption, or scattering of radiation and the selection rules governing the allowed transitions have been included in Table I. Thus for a

TABLE I.—ROTATIONAL ENERGY FORMULÆ AND SELECTION RULES FOR THE FOUR CLASSES OF POLYATOMIC MOLECULES.

Class of molecule.	Expression for rotational energy, $E_r$ .	Selection rules.	
		(a) Infra-red spectra.	(b) Raman spectra.
Linear $I_A = I_B$ ; $I_C = 0$	$\frac{h^2}{8\pi^2 I_A} J(J+1)$ $J = 0, 1, 2, \dots$	$\Delta J = \pm 1$	$\Delta J = 0, \pm 2$
Spherical $I_A = I_B = I_C$	$\frac{h^2}{8\pi^2 I_A} J(J+1)$ $J = 0, 1, 2, \dots$	No active transitions	No active transitions
Symmetrical top $I_A = I_B \neq I_C$	$\frac{h^2}{8\pi^2 I_A} J(J+1) + \left( \frac{1}{I_C} - \frac{1}{I_A} \right) \frac{K^2 h^2}{8\pi^2}$ $K \leq J$ ; $J = 0, 1, \dots$	$\Delta J = \pm 1$ $\Delta K = 0$	$\Delta J = 0, \pm 1, \pm 2$ $\Delta K = 0$
Asymmetrical top $I_A \neq I_B \neq I_C$	No simple explicit expression in terms of $J$ , the quantum number for total angular momentum.	$\Delta J = \pm 1$	$\Delta J = 0, \pm 1, \pm 2$

linear molecule the possible energy changes in the infra-red are given by:

$$\Delta E_r = J h^2 / 4\pi^2 I_A,$$

$$J = 1, 2, 3, \dots \quad (1),$$

and the corresponding spectral frequencies are:

$$\nu_r = \Delta E_r / h = J h / 4\pi^2 I_A,$$

$$J = 1, 2, 3, \dots \quad (2).$$

In other words the pure rotation spectrum of a linear molecule in the infra-red consists of a

number of equally spaced lines, the separation between the lines being inversely proportional to the moment of inertia of the molecule. The same is true of the Raman spectrum, only the separation between the lines is twice as great. Observation of these spectra, which is unfortunately technically difficult, would therefore yield a value for the moment of inertia of the molecule. In the case of spherically symmetrical molecules, such as methane or carbon tetrachloride, transitions between the levels do not

arise through emission, absorption, or scattering; consequently such molecules have no pure rotation spectra. This phenomenon might therefore be used as a test of spherical symmetry in the investigation of molecular structure. In the case of symmetrical-top molecules, such as ammonia or the methyl halides, the infra-red spectrum is of exactly the same type as in the linear molecule, and yields a value for one of the moments of inertia ( $I_A$ ). It is important to notice that no information can be obtained about the other moment of inertia ( $I_0$ ) from spacings in rotation spectra, because of the selection rule  $\Delta K=0$ . It is possible, however, to obtain information about the ratio  $I_0/I_A$  from the intensities of the lines. In the case of asymmetrical-top molecules, there is no explicit expression for the energy levels in terms of the moments of inertia, but the energy-level scheme may be computed in terms of these moments, provided certain algebraic equations can be solved. This means that the values of the three moments of inertia cannot be derived in a straightforward way. However, it is possible to obtain the values of the moments of inertia by a process of trial and error, by starting from probable values and computing an energy-level scheme. The trial values can then be modified until the computed energy levels agree with those derived from the spectrum. Frequently it is possible to obtain a fair approximation to the spectrum of an asymmetrical molecule in which the difference between two of the moments of inertia is small by treating it as a symmetrical-top molecule of which the levels have been perturbed, through the imperfection of the symmetry. The difficulties of the theory are further increased by the fact that distortion of the molecule takes place at high rotational energies through the action of centrifugal forces. In spite of these complications, the pure rotation spectrum of water vapour, which extends in the infra-red from  $15\mu$ . to beyond  $135\mu$ ., has been successfully observed and interpreted by Dennison, Randall, and others (Physical Rev. 1937, [ii], 52, 160; *ibid.* 1940, [ii], 57, 128) to yield highly accurate values for the moments of inertia and thus for the internuclear distances (O-H distance =  $0.9580 \text{ \AA}$ ., HOH angle =  $104^\circ 31'$ ).

It is unlikely, however, that pure rotation spectra will ever become an important tool in the elucidation of molecular structure. The experimental difficulties in obtaining these spectra (which will be discussed briefly in the section on experimental methods, p. 194b) are quite formidable, particularly under high resolving power, and most of the information obtained can equally well be derived from the vibration-rotation spectrum, which lies in a much more accessible region of the infra-red.

**Vibration-Rotation Spectra.**—The vibrational energy of any molecule is given by the expression:

$$E_v = (n_1 + \frac{1}{2})h\nu_1 + (n_2 + \frac{1}{2})h\nu_2 + \dots \quad (3),$$

where  $\nu_1, \nu_2, \dots$  are the "fundamental" frequencies of the molecule, and  $n_1, n_2, \dots$  are quantum numbers which may take any positive integral value. The number of fundamental

frequencies depends on the number of atoms in the molecule, there being in general  $3n-6$  fundamentals for a molecule containing  $n$  atoms. However, if the molecule is linear, the number of fundamentals is  $3n-5$ . These fundamental frequencies depend in turn on the masses of the atoms, the internuclear distances and angles, and the restoring forces brought into play when the atoms are displaced from their equilibrium positions in the molecule. Thus in the special case of a diatomic molecule, for which it is assumed that the restoring force is of a Hooke's Law type (i.e., an alteration of the equilibrium internuclear distance by an amount  $x$  causes a restoring force  $kx$  to come into play), the fundamental frequency is given by the equation:

$$\nu = (1/2\pi)\sqrt{\{k(m_1+m_2)/m_1m_2\}} \quad (4),$$

where  $m_1$  and  $m_2$  are the masses of the two atoms. Vibration-rotation spectra arise from transitions between the energy levels given by (3) through the emission, absorption, or scattering of radiation. Just as in the rotational case, the transitions are governed by selection rules, and these selection rules depend on the symmetry of the molecule. It is not possible in an article of this type to consider all the possible types of symmetry with their associated selection rules, but some general rules can be given which should make it clear how the analysis of vibration spectra enables a molecule to be assigned to a definite symmetry class.

The first of these general rules is that by far the most probable of the "allowed" transitions are those in which one of the quantum numbers changes by one unit while all the others remain unaltered. In other words, the most frequent energy changes in absorption or scattering correspond to certain of the fundamental frequencies,  $\nu_1, \nu_2$ , etc., of the molecule. The less frequent transitions in which a quantum number changes by more than one unit, or several quantum numbers change simultaneously, correspond to "overtone" ( $2\nu_1, 2\nu_2$ , etc.) or "combination" frequencies ( $\nu_1+\nu_2, \nu_2+2\nu_3, 2\nu_1+3\nu_2$ , etc.). This rule allows many of the fundamental frequencies to be identified with the most intense absorption or Raman frequencies, but it does not by any means solve the problem of determining all the fundamental frequencies of the molecule. It frequently happens that certain "allowed" fundamentals are relatively weak in absorption and scattering while some overtone or combination frequencies are stronger than these weakly active fundamentals.

The second rule is that fundamental frequencies will be active in absorption only when the mode of vibration of the molecule associated with that fundamental frequency causes an equiperiodic variation in the permanent electric moment of the molecule. Thus in Fig. 4, which represents the five fundamental modes of vibration of acetylene,  $\nu_1, \nu_2$ , and  $\nu_5$  are completely symmetrical modes which cause no variation in the permanent (zero) moment of this molecule. These three fundamentals will not appear in the infra-red spectrum, but  $\nu_3$  and  $\nu_4$  will give rise to absorption, as their unsymmetrical nature gives rise to an oscillating dipole-moment. If, however, one of the hydrogen atoms in

acetylene is replaced by a deuterium atom, all the vibrations become unsymmetrical and therefore active in absorption. The relative intensity of the different active fundamentals in absorption is directly related to the amplitude of the associated change in dipole moment. This explains why certain fundamentals, which may be "allowed" as far as symmetry conditions are concerned, may yet be very weak in intensity.

The third rule is that fundamental frequencies will be active in Raman scattering only when the mode of vibration of the molecule associated with that fundamental frequency causes an equiperiodic variation in the polarisability of the molecule. Thus on referring to the vibrations of acetylene in Fig. 4, it is seen that the three symmetrical frequencies  $\nu_1$ ,  $\nu_2$ , and  $\nu_5$  will cause the polarisability of the molecule to vary with the corresponding frequency, whereas the unsymmetrical frequencies  $\nu_3$  and  $\nu_4$  will cause

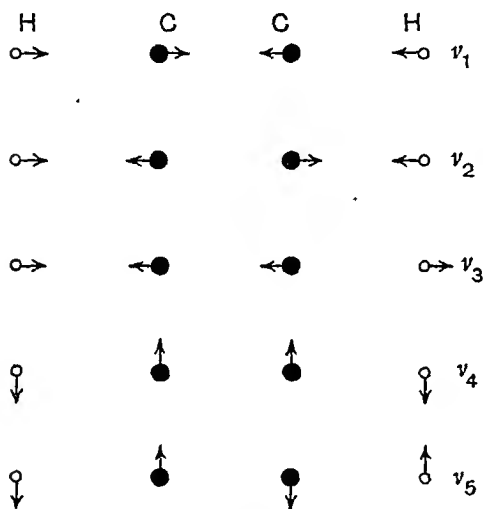


FIG. 4.

the polarisability to pass through two complete cycles for each complete cycle of either vibration. This may be grasped more readily if it is noticed that on starting from one extreme position of either  $\nu_3$  or  $\nu_4$  the configuration of the molecule after half of a vibration cycle is the same as that obtained by rotating the molecule through  $180^\circ$  about any line through the centre of gravity and perpendicular to the axis of the molecule. As the molecule is constantly rotating, the polarisability after half a cycle must be the same as it was at the beginning of the cycle; in other words the polarisability has completed its cycle of variation at double the fundamental frequency. This means that the overtones  $2\nu_3$  and  $2\nu_4$  may appear in the Raman spectrum although the fundamentals are forbidden.

It is clear that the application of these last two rules presupposes a knowledge of the physical character of the fundamental or "normal" modes of vibration of the molecule. How, for instance, were the normal modes of acetylene illustrated in Fig. 4 derived? Was it by the application of mathematical methods, or was it possible to use general physical argu-

ments? The answer is that in this particular case either method may be employed, but that the mathematical approach is the more fundamental. Any molecule may be regarded as a vibrating system made up of a number of atoms having a definite equilibrium configuration, determined by the interatomic forces. Now any vibrating system possesses a limited number of "fundamental" or "normal" modes of vibration, such that every possible vibration of the system can be built up out of these fundamentals or their overtones, while none of the fundamentals can be built up from any combination of the other fundamentals. The derivation of the physical nature of the fundamentals of any vibrating system is straightforward applied mathematics (see E. T. Whittaker, "Analytical Dynamics," Cambridge University Press, 1927) but the actual working out is very complicated, and special techniques have been developed for molecular vibrations; these cannot be dealt with in this article. The other method, which can only be employed in simple cases, is the physical method of building up the normal modes of the molecule out of the normal modes of simpler vibrating units within the molecule. This method does not give more than the general physical character of the fundamentals, but this is all that is required in order to establish their symmetry properties and corresponding selection rules.

As an illustration, the physical method may be applied to the acetylene molecule of Fig. 4. Consider the molecule to be built up from two CH groups. Each of these CH groups possesses a fundamental frequency, so the complete molecule will possess two "CH frequencies," one corresponding to the two CH fundamentals oscillating in phase with one another, the other corresponding to them oscillating out of phase. The former is  $\nu_2$ ; the latter is  $\nu_3$ . If the CH groups are regarded as two rigid groups, vibrating like a large diatomic molecule, the vibration being largely controlled by the forces of the  $C\equiv C$  bond, another of the fundamentals, viz.  $\nu_1$ , is obtained. Finally, if oscillations of the CH groups are considered which involve only motions of the atoms perpendicular to the axis of the molecule, the two groups may oscillate, either in phase ( $\nu_4$ ) or out of phase ( $\nu_5$ ). This gives the five fundamentals illustrated in Fig. 4. However, it was stated earlier that a linear molecule with  $n$  atoms should have  $3n-5$  fundamentals; this requires acetylene to have 7 fundamentals. The explanation of the apparent discrepancy is that  $\nu_4$  and  $\nu_5$  are "degenerate" modes of vibration, each vibration being really two vibrations which are physically indistinguishable. Thus  $\nu_4$  and  $\nu_5$  could equally well have been represented as motions in a plane through the molecule perpendicular to the plane of the paper. There is, however, nothing which distinguishes the first vibration plane from the second, and the motions of the atoms cannot in fact be regarded as confined to one plane or the other, although the motions can be resolved into components in these two planes as a matter of mathematical convenience. The phenomenon of degeneracy is therefore a consequence of the high symmetry of the molecule, and is of quite



frequent occurrence in simple symmetrical molecules. In addition to the cases of double degeneracy in which the motions of the atoms are isotropic in planes, it is possible to have cases of triple degeneracy in which three fundamentals have coalesced and the motions of the atoms are isotropic in space. For instance, the highly symmetrical molecule of methane possesses two triply degenerate fundamentals.

It should be added that the results of this physical method of classifying the normal modes of vibration through their symmetry properties can be obtained by a purely mathematical technique involving the theory of groups. By means of certain rules derived from group theory it is possible to write down immediately for any given molecule the classification of the fundamentals into groups having common symmetry properties, and therefore obeying the same selection rules. Further, it is possible to state the degree of degeneracy of any fundamental, whether it will be active in absorption or in scattering, and in the latter case, to

predict some of the polarisation properties of the Raman frequencies. Details of this method, which cannot be included here, are now available in several publications (*e.g.*, Rosenthal and Murphy, *Rev. Mod. Physics*, 1936, 8, 317). It might appear from this that the physical method is of no value, as it only enables a few of the simpler cases to be dealt with, whereas the group-theoretical method is absolutely general. The physical method, however, has the advantage that it gives some indication of the magnitude of the frequencies and this is of considerable value in correlating the observed absorption and Raman frequencies with the particular normal modes of vibration of the molecule. For instance, the fundamental frequency of a CH group is always in the neighbourhood of 3,000  $\text{cm}^{-1}$ , irrespective of the nature of the molecule; the frequency of an OH group is always near 3,600  $\text{cm}^{-1}$ , and so on. The explanation is that the vibration is almost entirely confined to the light hydrogen atom and is therefore practically independent of the rest of the mole-

Infra-Red Spectrum	Raman Spectrum	X	Y	X		X	Y	X	Infra-Red Spectrum	Raman Spectrum
Active	Active				$\nu_1$				Inactive	Active
Active	Active				$\nu_2$				Active	Inactive
Active	Active				$\nu_3$				Active	Inactive

(a) Non-Linear Case

(b) Linear Case

Fig. 5.

molecule, its magnitude being controlled primarily by the value of the force constant of the bond holding the hydrogen to the rest of the molecule. This can be verified by taking  $m_1$  very much greater than  $m_2$  in equation (4) above, when the expression for the frequency of the diatomic group reduces to  $\nu = (1/2\pi)\sqrt{(k/m_2)}$ . The extension of this to frequencies other than those involving the motions of hydrogen atoms has to be done with some caution. Although certain bonds, such as N=N, C=C, C $\equiv$ C, C=O, C=N, and C $\equiv$ N, may frequently be correctly associated with fundamental frequencies in polyatomic molecules in the neighbourhood of 2,200, 1,650, 2,000, 1,750, 1,650, and 2,100  $\text{cm}^{-1}$ , respectively, because the vibration of the bond in question is fairly independent of the rest of the molecule, this cannot be taken as true in general. The fundamental frequencies of any molecule are frequencies of the molecule as a whole and it is only in the case of the hydrogen frequencies that the large difference in mass localises the fundamental with certainty in a particular bond.

Before going on to discuss the application of

the above rules to a few illustrative examples mention may be made of one other general empirical rule governing the magnitudes of fundamental frequencies. It is that frequencies which principally involve *stretching* of bonds are greater than those which are associated with the *deformation of angles* between the same bonds. Thus for acetylene in Fig. 4 the frequencies  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  will be greater than  $\nu_4$  and  $\nu_5$ . Of course it may not always be possible to make this sharp distinction between a "bond frequency" and a "deformation frequency," which can be done in a linear molecule, but frequently it will be found that this division can be made, and is of value in assigning observed frequencies to the appropriate mode of vibration.

**Application of Symmetry Selection Rules to Simple Molecules.**—Suppose the infra-red and Raman spectra of a triatomic molecule  $YX_2$  have been observed, what deductions can be made from them regarding the configuration of the molecule? The normal modes of vibration may be considered first. These are illustrated in Fig. 5, which also includes the selection rules for infra-red and



Raman spectra for the two possible configurations. The selection rules are so different in the two cases that it should be possible to state immediately whether the molecule is linear or not. In the non-linear case all three fundamentals will appear in absorption and in Raman spectra, whereas in the linear case only the two unsymmetrical fundamentals  $\nu_2$  and  $\nu_3$  will appear in absorption and only the symmetrical frequency  $\nu_1$  will appear in the Raman spectrum. It will be noticed that in the linear case the infra-red and Raman spectra are complementary, and it may be remembered that this was also the case in acetylene (Fig. 4). These are, in fact, special cases of a general rule which states that in a molecule possessing a centre of symmetry, all fundamentals which are unaltered by a reflection of all the co-ordinates in the centre of symmetry will be active in the Raman spectrum but inactive in the infra-red, whereas the opposite will hold for fundamentals which are "antisymmetrical" towards a reflection in the centre of symmetry. In this connection "antisymmetrical" means that the phase of the vibration has been altered by half a complete period by reflection in the centre of symmetry.

The application of this last rule makes it possible to determine, from inspection of the infra-red and Raman spectra of a  $YX_3$  molecule, whether the configuration is planar (as, for example, in the  $NO_3^-$  ion) or pyramidal (as in the ammonia molecule). It has also been applied to confirm the hexagonal symmetry of the benzene molecule.

The  $YX_4$  class of molecules may have either a pyramidal or a tetrahedral configuration. Here again the selection rules based on the different symmetry properties are entirely different and allow an immediate decision to be made between the two configurations. In a similar way it is possible to prove very easily whether molecules belonging to the  $Y_2X_4$  class are planar and symmetrical, or have the  $YX_2$  groups at right-angles to one another, and so on. Sometimes the symmetry selection rules have been very valuable in proving that a particular molecule has an unsymmetrical structure. Examples are ozone (which cannot be equilateral), and hydrogen peroxide and hydrazine (both of which have very skew configurations). An extension of the same method allows a distinction to be made between the *cis*- and *trans*-forms of a compound; similarly the existence of free or restricted rotation may be established in favourable cases. One drawback in all this work is that the symmetry selection rules are strictly valid only for the vapour state, and Raman spectra are extremely difficult to obtain under such conditions. Even the infra-red absorption may present considerable difficulties when the boiling-point is over  $100^\circ C$ .

**Rotational Fine Structure and Moments of Inertia.**—When the vibration spectrum has been obtained in the vapour state, there is always an extensive fine structure due to the changes in rotational energy which accompany the change in vibrational energy. As the detailed interpretation of this fine structure is too complex to be given here, only the main results will be discussed. The formulæ for the

rotational energy have already been given in the section on pure rotation spectra; the selection rules are, however, not quite the same, and differ according to the type of vibrational transition involved. Thus in the case of a linear molecule,  $\Delta J = \pm 1$  for vibrations parallel to the axis of the molecule (such as  $\nu_3$  in Fig. 4), whereas  $\Delta J = 0, \pm 1$  for vibrations perpendicular to the axis of the molecule (such as  $\nu_4$  in Fig. 4). The transitions  $\Delta J = \pm 1$  give rise to a series of equally spaced lines on either side of the vibration frequency  $\nu$ , the frequency separation between the lines being  $h/4\pi^2 I$ ; these are known as the "P" and "R" branches of the band. The transition  $\Delta J = 0$  in the "perpendicular" vibrations gives rise to a "Q" branch coinciding with the vibration frequency. The presence or absence of this Q branch is useful in assigning bands to the correct mode of vibration; the separation between the lines in the P and R branches can be used to evaluate the moment of inertia,  $I$ , of the molecule. Only in the special case of the  $YX_3$  molecule is it possible to calculate the internuclear distances. If, however, an isotopic form of the molecule is also studied (e.g., acetylene with one or more deuterium atoms in place of hydrogen), then from the two moments of inertia all the internuclear distances can be obtained. The limiting factor in the application of this method to the determination of moments of inertia lies in the resolving power attainable in the infra-red. Because of the small amount of energy available, it is extremely difficult to use slits sufficiently narrow to resolve rotation lines closer than  $0.5 \text{ cm}^{-1}$ . This means that in general molecules with moments of inertia greater than  $10^{-38} \text{ g.-cm}^2$  will not have the rotational fine structure sufficiently well defined to allow an accurate estimate of the line spacing to be made. The heaviest linear molecule to have its structure resolved so far is  $CS_2$  with a moment of inertia of  $247 \times 10^{-40} \text{ g.-cm}^2$ , but it should be added that the spacing here is twice the normal, as the absence of nuclear spin in the sulphur atom causes alternate lines in the spectrum to be missing. It is likely that as advances continue to be made in the technique of infra-red spectrography, this limit will be considerably surpassed. A new limit will then be reached, set by the natural width of the absorption lines themselves.

In the case of spherical molecules the structure of each band is exactly the same as for the "perpendicular band" of a linear molecule, but the spacing between the lines varies from band to band and is not a simple function of the moment of inertia. This is due to the existence of internal angular momenta in the molecule, arising from the vibrational motions. Allowance can be made for this effect and accurate values finally derived for the moment of inertia. The only molecules which have so far been investigated are methane, silane, and germane. For symmetrical-top molecules both moments of inertia can be evaluated, although complications occur in determining  $I_0$ , again through internal angular momenta. The only molecules in this class reasonably fully investigated are  $CH_3F$ ,  $CH_3Cl$ ,  $NH_3$ ,  $PH_3$ , and  $BF_3$ . Here again the study of deuterium compounds is often helpful

in the deduction of internuclear distances from moments of inertia. The asymmetrical-top molecules present serious difficulties as noted already in the discussion of pure rotation spectra. The line spacings and intensities are quite irregular, and the unravelling of the whole structure is a task of extreme difficulty even for the most experienced spectroscopist. In cases where the degree of asymmetry is small the structure will not differ fundamentally from that in a symmetrical-top molecule, and here the moments of inertia can be evaluated with much less difficulty. The following are the only asymmetrical-top molecules of which the infra-red spectra have been successfully analysed to give reliable values for the moments of inertia:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{C}_2\text{H}_4$ .

Summarising, it may be said that although in theory the analysis of the rotational fine-structure of infra-red vibration spectra of any molecule should yield values for the moments of inertia of that molecule, the method has so far been applied to some thirty molecules, and the prospect of extending this list appreciably is small unless some advance is made in spectroscopic technique which will provide greater resolving power. Even with increased resolving power, the difficulties in unravelling the complex structure of the more asymmetrical molecules are formidable. This rather depressing conclusion has led investigators to consider whether information on the structure of the molecule, further than that provided by the symmetry selection-rules, can be obtained purely from the vibration spectra in which the rotational fine structure is unresolved or only partially resolved. In the case of partial resolution it is often possible to give approximate values for the moments of inertia by a natural extension of the theories already developed for complete resolution, but when the rotational structure is entirely absent (*e.g.*, in the case of molecules examined in the liquid or solid state) a different approach has to be made. This involves a consideration of the force constants governing the stretching of the chemical bonds in the molecule, and the relation of these to the internuclear distances on the one hand, and to the vibrational frequencies of the molecule on the other.

**Force Constants and Internuclear Distances.**—When any molecule vibrates, several forces come into play tending to restore the atoms to the positions they occupy in the vibrationless state of equilibrium. The exact nature of these forces is very complex, and only in a few extremely simple cases has it been possible to overcome the mathematical difficulties encountered when the methods of quantum mechanics are applied to the system of electrons and nuclei making up the molecule. If, however, the molecule is regarded as a collection of masses (atoms), held together by simple elastic forces, such that any alterations in internuclear distances of the chemical bonds or of the angles between two bonds bring into play forces which are proportional to the displacements of the bond lengths or bond angles from their equilibrium values, then the methods of classical mechanics may be employed and the problem becomes much more tractable. In particular, it

is possible to derive simple algebraic equations connecting the force constants of the bonds and bond angles with the masses of the atoms and the fundamental frequencies of the molecule. The triatomic molecule  $\text{YX}_2$  (Fig. 5) is a simple example and may be regarded as having bonds between the Y atom and each of the X atoms, characterised by a force constant  $K$  exactly analogous to the force constant  $k$  of the diatomic molecule of equation (4); displacements of the  $\text{YX}_2$  angle from its equilibrium value are opposed by another force characterised by  $K_\alpha$ . The equations connecting these force constants with the frequencies  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and the masses  $m_Y$ ,  $m_X$  are then as follows:

$$K = m_X m_Y \nu_3^2 / \{m_Y + 2m_X \sin^2(\alpha/2)\} \quad (5).$$

$$K_\alpha = m_X \nu_1^2 \nu_2^2 (XY)^2 \{m_Y + 2m_X \sin^2(\alpha/2)\} / \nu_3^2 (m_Y + 2m_X)^2 \quad (6).$$

$$m_X (\nu_1^2 + \nu_2^2) = (K/m_Y) \{m_Y + 2m_X \cos^2(\alpha/2)\} + \{2K_\alpha/m_X (XY)^2\} \{m_Y + 2m_X \sin^2(\alpha/2)\} \quad (7).$$

Provided the angle  $\alpha$  between the two  $\text{YX}$  bonds is known, the first equation gives the value of the force constant  $K$  of the bond: provided the  $\text{XY}$  distance is known, the second equation gives a value for  $K_\alpha$ , while the third equation may be used as a test of the assumptions by substituting the values for  $K$  and  $K_\alpha$  found from the first two equations. Tests of this kind usually show that the simple assumption of valency forces is not entirely satisfactory and in some cases may be quite unjustified. It is generally found necessary to introduce additional forces which allow for interaction between various parts of the molecule. Thus in the triatomic molecule it may be necessary to assume that alteration of the length of the  $\text{XY}$  bond simultaneously causes an alteration in angle between the  $\text{XY}$  bonds. Unfortunately, when interaction terms of this type have to be introduced, it becomes impossible to get any check on the assumptions, for there are as many, or sometimes more, unknown force-constants than there are equations from which to determine them. In spite of these difficulties it has been possible to get fairly reliable values for the force constants of many of the commoner chemical bonds. Single bonds usually have values ranging from 2 to  $7 \times 10^5$  dynes per cm.; double bonds lie roughly between 7 and  $12 \times 10^5$  dynes per cm., while triple bonds may have values greater than  $20 \times 10^5$  dynes per cm. It is possible by this means to tell when a bond is not simple but is a resonance hybrid. For example, the  $\text{C}-\text{C}$  force constant in benzene has the value  $7.5 \times 10^5$  dynes per cm., whereas the  $\text{C}-\text{C}$  single-bond force-constant has a value close to  $5 \times 10^5$  dynes per cm., and the double-bond force-constant is between 9 and  $10 \times 10^5$  dynes per cm.

The force constant of a chemical bond is therefore just as much a property of that particular bond as the internuclear distance between the two atoms, and several workers have shown that there is a very close relation between these two quantities. One form of relation, due to Douglas-Clark (Trans. Faraday Soc. 1941, 37, 293) may be quoted here:

$$k_e r_e^3 n = k_{gr} \quad (8),$$

where  $k_e$  is the force constant of the bond for displacements from equilibrium,  
 $r_e$  is the equilibrium internuclear distance,  
 $n$  is a group number, defined as the sum of the valency electrons in each atom,  
 and  $k_{qr}$  is a sub-period constant, depending on the positions of the atoms in the Periodic Table.

This opens up another method of determining internuclear distances from vibration spectra. At present it does not compare in accuracy with the method deriving from the analysis of rotational fine structure, partly because of the above-mentioned difficulties in evaluating the force constants accurately, and partly because of the empirical nature of the equations, such as (8), relating the force constant to the bond length. However, much useful information has already been obtained by this method, and it is capable of extensive development. It offers the only prospect of dealing with large molecules, in which the moments of inertia depend on so many internuclear distances and angles that even although analysis of the rotational fine structure could be carried out, and the moments of inertia evaluated, this might not materially assist in settling the structure of the molecule.

**Detection of Hydrogen Bonds.**—Suppose a molecule contains a hydrogen atom H which is attached not only to some atom X in that molecule, but also to a second atom X' which may or may not be in the same molecule. In the first case there is an internal hydrogen bond; in the second, two molecules are loosely bound together through an external hydrogen bond. Examples of the two types are found, respectively, in o-chlorophenol and acetic acid. The existence of these hydrogen bonds can be very readily detected from the vibration spectra of the molecules. It has already been remarked that the OH group has a fundamental frequency in the neighbourhood of  $3,600\text{ cm}^{-1}$ , in which the motion is almost entirely confined to the H atom and so is virtually independent of the rest of the molecule. If, however, this H atom is now to take part in the formation of a hydrogen bond, the original O—H bond will be weakened by the formation of the H—X' bond. This means that the O—H distance will be increased and consequently the O—H force constant decreased, giving as a result a considerable lowering of the characteristic OH fundamental frequency. The fundamental absorption band of the OH group is shifted from the usual position around  $3,600\text{ cm}^{-1}$  to anywhere between  $3,450\text{ cm}^{-1}$  and  $3,100\text{ cm}^{-1}$ , according to the strength of the hydrogen bond. Such a displacement is very easily observed. In this manner the existence of hydrogen bonds has been established in many cases where evidence has been unobtainable by other means. More generally, alterations in vibration frequencies may be used as a tool in the investigation of inter- as well as intra-molecular forces.

#### EXPERIMENTAL.

**Infra-red Spectra.**—The range covered by the infra-red is so large that one technique cannot be used to cover all of it. Any suitable

spectrograph used for the visible region can be employed for that part of the infra-red which can be recorded by photographic methods. Unfortunately this is an extremely small portion of the infra-red (see Fig. 1) and contains no fundamental frequencies. It extends from the end of the visible red, about  $7,500\text{ Å}$ . or  $13,333\text{ cm}^{-1}$ , to about  $1.3\mu$ . or  $7,690\text{ cm}^{-1}$ . Quite useful information can often be obtained from the overtone and combination frequencies that fall in this region, although these are in general more complex in structure than the fundamentals, and so more difficult to interpret. Between  $1.3$  and  $3.5\mu$ . ( $7,690\text{ cm}^{-1}$  and  $2,875\text{ cm}^{-1}$ ) a spectrometer with a quartz prism gives sufficient resolving power for most purposes, although a grating has to be used to get the best results. For these, as for all longer wave-lengths, the radiation is normally detected by means of a thermocouple or some other thermo-electric device. Between  $3.5\mu$ . and  $17\mu$ . ( $2,857\text{ cm}^{-1}$  to  $588\text{ cm}^{-1}$ ) the usual dispersing agent is a rock-salt prism, but synthetic lithium fluoride and calcium fluoride (which have higher dispersive power from  $3$  to  $6\mu$ . and  $6$  to  $10\mu$ ., respectively) are now becoming available. In order to get beyond  $588\text{ cm}^{-1}$  the rock salt prism must be replaced by one of sylvine, which, beyond  $400\text{ cm}^{-1}$ , is in turn replaced by one of potassium bromide. The limit of transmission of potassium bromide is about  $300\text{ cm}^{-1}$ . In all of this region covered by the rock salt, sylvine, and potassium bromide prisms, it is essential to supplement the dispersion of the prism with a grating if the highest resolving power is desired, but the dispersion given by the prisms alone is usually sufficient to reveal all but the finer details of rotational fine-structure and hence for all work on liquids and solids. Until quite recently it was customary to plot infra-red spectra point by point, the observer noting the amount of infra-red radiation indicated by the thermocouple at each wave-length, with and without the absorbing molecules in the path of the radiation, and computing the percentage absorption for that wave-length. Several methods of recording infra-red spectra have now been developed which should reduce the labour involved and at the same time greatly accelerate the whole technique. Most of these recording methods suffer from the drawback that the record obtained is not a direct record of the percentage absorption but a record of the amount of energy transmitted by the material at the various wave-lengths. Since the incident energy varies between the different wave-lengths especially in regions of atmospheric absorption the records have to be reduced to give percentage absorption by comparison with a record of the incident energy. This drawback is not serious when qualitative work is concerned, but for quantitative work it is preferable to use the double beam method introduced by Hardy, in which percentage absorptions are directly recorded. It should be added that it is now possible to scan portions of the infra-red sufficiently rapidly to allow spectra to be examined visually on a cathode ray screen.

**Raman Spectra.**—In order to obtain satisfactory Raman spectra it is essential to have a

powerful source of monochromatic radiation, and accurate alignment of the apparatus so that the maximum amount of scattered light and the minimum amount of reflected light enters the analysing spectrograph; the latter should be of aperture sufficiently large to keep exposures within a reasonable time limit of a few hours without sacrificing resolving power so that frequencies lying close together are not separated. In general, the most suitable source of monochromatic radiation is a mercury arc in which the particular exciting frequency has been isolated by a filter. The following wave-lengths have all been used successfully: 5,791 Å., 5,770 Å. (yellow), 5,461 Å. (green), 4,358 Å. (blue), 4,047 Å. (violet), 3,650 Å. and 2,536 Å. (ultra-violet), but especially that at 4,358 Å. It is preferable to use a wave-length as far into the ultra-violet as possible, since the intensity of the scattered light is inversely proportional to the fourth power of the wave-length, but in many cases ultra-violet light causes decomposition. Again, the substance under examination may possess absorption bands in all but the green or yellow regions of the spectrum. A helium lamp giving monochromatic radiation of wave-length 3,888 Å. has also been used, but it is not so easy to construct as the mercury lamp. An arc with a tin-cadmium alloy has also been used to produce monochromatic radiation in the red end of the spectrum for use with certain coloured materials. Spectrographs have been specially designed by most of the optical firms for the observation of Raman spectra. It is seldom advisable to work with an aperture ratio less than  $f/5$ . It is a good plan to have alternative cameras of different aperture so that the fast one can be used for substances with very weak Raman spectra, while the longer-focus camera can be used with strongly scattering substances in order to get maximum resolving power.

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G. B. B. M. S.

**MOLECULAR SPECTRA (VISIBLE AND ULTRA-VIOLET).**—The study of light emission and absorption by molecules concerns the simplest diatomic entities as well as molecules of many of the most complicated organic substances. It makes use of a considerable variety of experimental techniques adapted to the investigation of emission, absorption, and fluorescence, exhibited by gases, vapours, liquids, solids, and solutions. The data obtained may be valued as material for the detailed description of molecular structure in terms of the more abstruse theories of mathematical physics, or, on the other hand, the results may be used entirely empirically. Between these two extremes lies a considerable territory where technical limitations give rise to semi-empirical and tentative interpretation. At each level of study the investigator needs to be versed in some other discipline, mathematical, physical, or chemical, and any general account will reflect the bias of its author.

In this article the first aim will be a simplified account of the application of the quantum theory to the spectra of simple molecules. The second aim will be to illustrate the way chemists have sought to interpret the data on larger molecules—usually in the dissolved state—and the third aim to give examples of spectra applied to constitutional problems.

In the visible and ultra-violet regions molecular spectra arise primarily because of electronic energy changes. These quantised transitions are not usually very numerous, but the energy of the molecule is also affected by quantised vibrational energy contributions. The observed spectra may then appear to be very complex.

The theory follows naturally from the treatment of atomic spectra.

## THEORY OF SIMPLE BAND SPECTRA.

Electronic energy levels for the isolated hydrogen atom are given by:

$$E_n = -Rhc/n^2,$$

where  $R = 2\pi^2me^4/h^3c$  and  $n$  has integral values 1, 2, 3, . . . An absorption frequency  $\nu = Rc\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$  occurs when  $n$  changes from 1 to 2, and an emission frequency when  $n$  changes from 2 to 1. If hydrogen atoms fall to the levels  $n=1$  or 2 from higher levels, series of lines occur (in emission):

$$\nu = Rc\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \text{ (Lyman Series),}$$

$$\nu = Rc\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \text{ (Balmer Series), etc.}$$

Analogous molecular processes of electronic excitation occur, and for simple molecules it is possible to identify the transitions involved. Even with polyatomic molecules useful approximations can be made.

Two processes which do not occur with single atoms enhance both the complexity and significance of molecular spectra; they are:

(a) energy intake resulting in intramolecular vibration of constituent atoms;

(b) energy intake affecting the whole molecule in respect of its rotation about some axis.

Vibrational and rotational changes, like electronic transitions, are quantised, and quantum numbers  $v$  and  $J$  are used to characterise vibrational and rotational states, respectively. The energy of a molecule will then be determined as a sum of three terms:

$$E(n, v, J) = E_n + E_v + E_J.$$

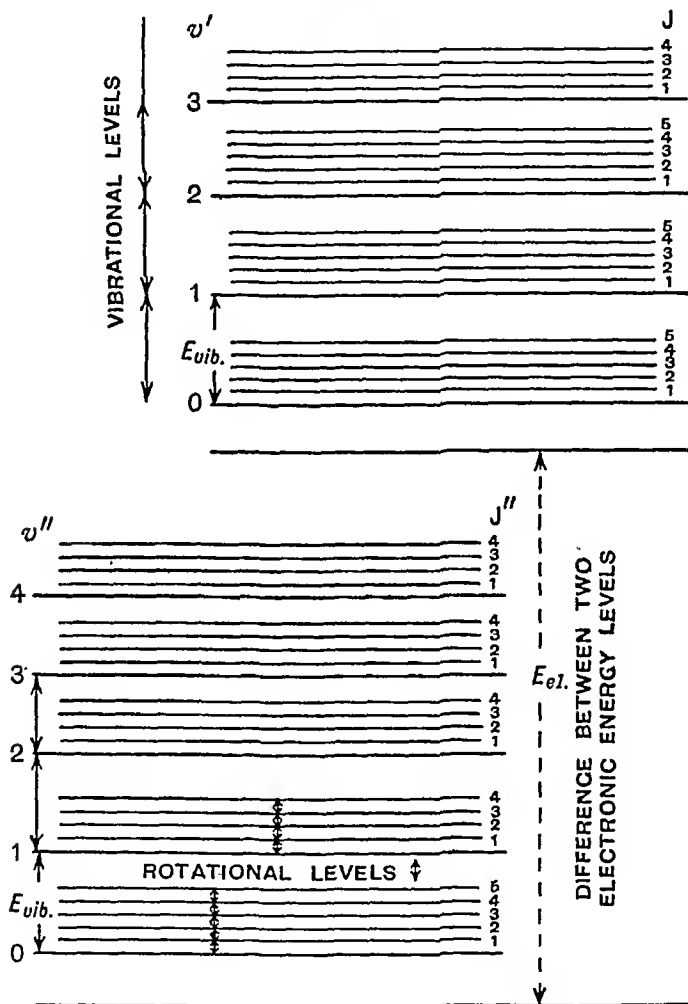


FIG. 1.

In general,  $E_n$  is very much greater than  $E_v$ , which in turn is much larger than  $E_J$ , so that  $v_{el} \gg v_{vib} \gg v_{rot}$ . (see Fig. 1).

$$(\Delta E_{el} = 20-200 \text{ kg.-cal. per g.-mol.})$$

$$\Delta E_{vib} = 1-10 \text{ kg.-cal. per g.-mol.}$$

$$\Delta E_{rot} = \text{ca. } 0.1 \text{ kg.-cal. per g.-mol.})$$

The high frequency of the electronic motion corresponds with the very small mass of the electron, just as the slower motion of the atoms is due to their greater mass, and, in consequence, the swiftly moving electrons can be regarded as occupying at any instant the optimum position

consistent with quantum conditions. It follows that each electronic state of the molecule is linked with a defined vibrational quantum corresponding with a fundamental vibration "frequency,"  $\omega_0$ . ( $\omega_0 = h\nu_0$ .) The energy,

$$E_{vib}/h = (v + \frac{1}{2})\omega_0,$$

the  $\frac{1}{2}$  being an introduction of the newer quantum-theory to include zero-point energy. Actual molecules are not perfect harmonic oscillators, and the corrected equation

$$E_{vib}/h = (v + \frac{1}{2})\omega_0 - (v + \frac{1}{2})^2 x_0 \omega_0 + \dots$$

gives better results.

In the case of a diatomic molecule AB with nuclei of masses  $m_1$  and  $m_2$  with an equilibrium nuclear separation  $r_e$ , for small values of  $\Delta r_e$  the force tending to restore the atoms to  $r_e$  varies as  $\Delta r_e$ , i.e.,  $F=k(r-r_e)$ , and the potential energy is  $V=(k/2)(r-r_e)^2$ , zero potential being taken as that obtaining when  $r=r_e$ . For a simple harmonic oscillator,

$$E_{\text{vib.}}=(v+\frac{1}{2})h\nu_0, \text{ where } \nu_0=(1/2\pi)\sqrt{(k/m)}$$

$$\text{with } m=m_1m_2/(m_1+m_2) \text{ (reduced mass).}$$

A limit is set to the increase in vibrational energy, in units  $h\nu_0$  as  $v$  increases, by the dissociation of the molecule into atoms. Anharmonicity as  $v$  increases can be fitted into a series :

$$V=(k/2!)(r-r_e)^2+(k'/3!)(r-r_e)^3+(k''/4!)(r-r_e)^4 \dots,$$

but it is more convenient to use the exponential form :

$$V=D[1+e^{-2a(r-r_e)}-2e^{-a(r-r_e)}]$$

(P. M. Morse, Physical Rev. 1929, [ii], 34, 57), whence :

$$E_v=(v+\frac{1}{2})h\nu_0-X_e(v+\frac{1}{2})^2h\nu_0 \dots,$$

if

$$\nu_0=(a/2\pi)\sqrt{(2D/m)} \text{ and } X_e=h\nu_0/4D$$

and  $D-\frac{1}{2}h\nu_0=D_0$  (actual dissociation energy).

The study of molecular structure is made easier by the use of potential-energy curves (see Fig. 2).

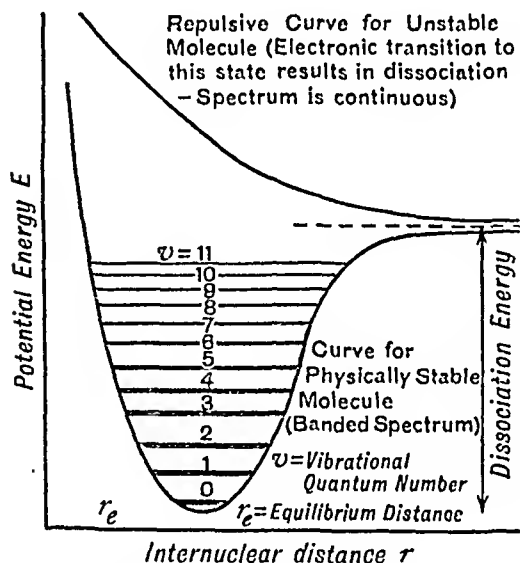


FIG. 2.—POTENTIAL-ENERGY CURVES FOR A DIATOMIC MOLECULE.

Consider two atoms separated by a large distance; if they come closer, repulsions between the nuclei bring about an increase in the potential energy of the system, and if the respective electronic configurations are unfavourable to combination this increase will be enhanced. If, however, the electronic configurations favour combination, there will be a decrease in potential energy. The potential energy curve obtained by summation of nuclear repulsions and elec-

tronic interactions will show a minimum when there is molecule formation. If the curve  $V/r$  shows no minimum the "molecule" is physically unstable. A physically stable molecule leaves the state represented by the minimum only by absorption of radiation or by collisions. If the molecule fails to survive collisions with others of its own kind it is chemically unstable (CH, SO, etc.). Each separate electronic state of a molecule possesses its own potential-energy curve, the differences between the minima corresponding with the energies of the different electronic transitions. As  $r$  (internuclear separation) increases, each curve approaches a horizontal line corresponding with dissociation. The electronic state with the lowest minimum is called the ground state of the molecule. The curve shows the amplitude of the atomic vibration for successive values of  $v$ , and the vibrational levels gradually converge to the limiting value of the energy shown in the horizontal part of the curve. If  $\Delta E_v$  is known for smaller values of  $v$  to be steadily decreasing, the curve  $\Delta E_v/v$  may be extrapolated to  $\Delta E_v=0$  at  $v_{\text{max.}}$ . Thus for a covalent molecule splitting into two neutral atoms, the number of vibrational levels is finite and the true energy of dissociation from

the vibrationless level  $v=0$  is  $D_0=\sum_{v=1}^{v_{\text{max.}}} \Delta E_v$ . Since

the vibrating atoms necessarily spend a large part of the time near extremes of  $r$ , an electronic transition is most frequent from such states. According to the Franck-Condon Principle  $r$  will be unchanged when the electronic transition occurs, and will correspond with an extreme of a vibration in the new state (Fig. 3). It follows therefore that there is no change in  $r_e$  on electronic excitation if absorption occurs from  $v''=0$  to  $v'=0$ ,  $v''=1$  to  $v'=1$ , etc. If, however, experiment shows that the most intense bands are from  $v''=0$  to  $v'=0$  and  $v''=0$  to  $v'=\text{say } 4$ , the internuclear distance  $r_e$  will be appreciably changed as a result of electronic excitation.

In addition to vibrating along the line joining the nuclei, a diatomic molecule may rotate about an axis perpendicular to this line and passing through the mass-centre of the molecule. The rotation is subject to quantum restrictions given by :

$$v_{\text{rot.}}=BJ(J+1),$$

where  $B=h/8\pi^2mr_e^2$  and  $J$  is the rotational quantum number, the physical meaning of which is that  $J(J+1)h^2/4\pi^2$  is the square of the angular momentum of the nuclear rotation.

When allowance is made for stretching under centrifugal action,

$$v_{\text{rot.}}=(h/8\pi^2I)J(J+1)+DJ^2(J+1)^2,$$

$$D \ll B, \quad h/8\pi^2I=B,$$

where  $I$  is moment of inertia. Experience shows that there is a selection principle according to which  $J$  can only change by 0 or  $\pm 1$ , i.e., the possibilities are :

$$J \rightarrow J+1$$

$$J \rightarrow J$$

$$J \rightarrow J-1.$$

If  $J'$  and  $J''$  represent two values of  $J$  allowed by the selection rule :

$$\nu_{\text{rot.}} = \nu_{\text{el.}} + \nu_{\text{vib.}} + B'J'(J'+1) - B''J''(J''+1)$$

(correction terms being neglected).

$B'$  and  $B''$  differ because the value of  $I$  changes with the change in  $r_e$ .

Writing  $\nu_0$  for  $\nu_{\text{el.}} + \nu_{\text{vib.}}$ , the equation becomes:

$$(a) \quad J' = J'' + 1; \\ \nu = \nu_0 + B'J'(J'+1) - B''(J'-1)J' \text{ or} \\ \nu = \nu_0 + J'(B' + B'') + J'^2(B' - B''),$$

where  $J' = +1, +2, +3$ , etc. This is called the *positive* or *R branch* (see Fig. 4).

$$(b) \quad J' = J'' - 1; \\ \nu = \nu_0 - J''(B' + B'') + J''^2(B' - B''),$$

where  $J'' = +1, +2, +3$ , . . . This is the *negative* or *P branch*.

$$(c) \quad J' = J''; \\ \nu = \nu_0 + J(B' - B'') + J^2(B' - B''),$$

where  $J = 0, 1, 2, 3$ , . . . This is the *zero* or *Q branch*.

In analysing spectra it is useful to note that the equation

$$\nu = \nu_0 + aJ + bJ^2 \text{ covers the } P \text{ and } R \text{ branches}$$

( $J = +1, +2$  . . . , *R branch*;  $J = -1, -2$  . . . , *P branch*;  $a = B' + B''$ ;  $b = B' - B''$ , leading quite simply to values for the moments of inertia).

One of the most obvious phenomena in the study of these spectra is the existence of band "heads," i.e., the crowding together of lines, in the direction of either longer or shorter wavelengths, to a sharply defined limit. This is accounted for as follows: let  $B'$  be  $> B''$ , so that  $a$  and  $b$  are both positive. If  $J$  is negative (*P branch*),  $aJ$  will be negative and  $bJ^2$  positive, and the quantity  $aJ + bJ^2$  will at first decrease and then increase as  $J$  rises. If, however,  $J$  is positive, the frequencies will increase steadily with increasing  $J$ , and the *R branch* will have no head. When  $B'$  is  $< B''$  the *R branch* will

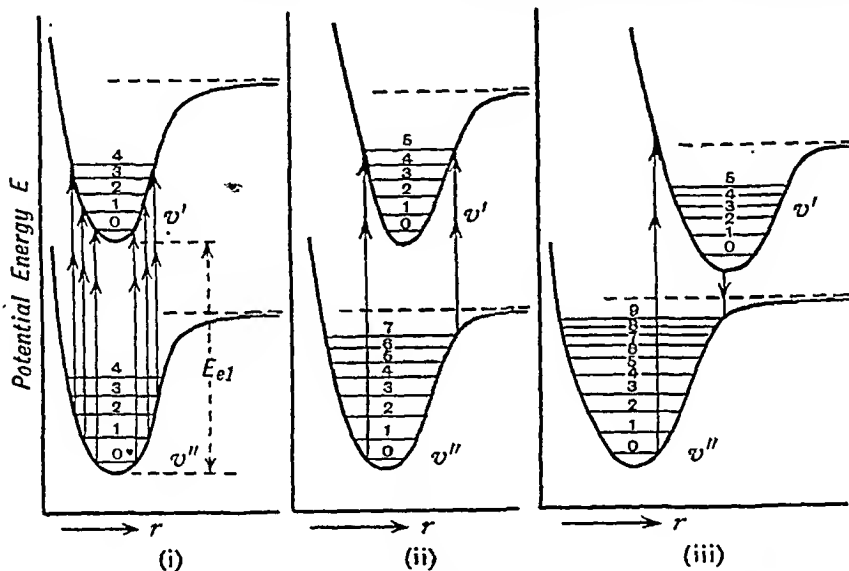


FIG. 3.

Case (i):  $r_e$  approximately the same for both electronic states. Band system will show a strong sequence of bands (0, 0), (1, 1), (2, 2), etc.

Case (ii):  $r_e$  slightly different in the two states. If  $v' = 5$  the strongest bands will be (5, 0) and (5, 7).

Case (iii):  $r_e$  considerably different in the two electronic states. Spectrum shows long progressions: (a) in emission  $v' = 0$  progression is strong; (b) in absorption.

now show the head, degrading in this instance to the red.

In sub-atoms an electron of azimuthal quantum number  $l$  has an orbital angular momentum of  $(\hbar/2\pi)\sqrt{l(l+1)}$ , and when there are several electrons, each with its own value for  $l$ , the resulting momentum  $L$  can have a number of values. The total angular momentum for the atom ( $J$ ) is the vector-sum of  $L$  and  $S$ , the sum of the electron spins. The multiplicity of  $J$  values is given by  $2S+1$ . In a simple molecule there is a strong field along the internuclear axis, and for each electron the value of  $l$  and of its component along the axis ( $\lambda$ ) play an important part. Atomic  $S$  electrons become  $S\sigma$  electrons if  $l=1$  and  $\lambda=0$ ,  $P$  electrons become  $P\sigma$ ,  $l=1$ ,  $\lambda=0$ , or  $P\pi$ ,  $l=1$ ,  $\lambda=1$ , etc.

The vector sum  $A$  for two or more electrons

gives the component of  $L$  along the molecular axis.

$L (A)$ .	Atoms.	Molecules.
0	$S$	$\Sigma$
1	$P$	$\Pi$
2	$D$	$\Delta$

The resultant spin angular momentum for all electrons provides a second quantum number  $S$ .

$S$ .	State of molecule.
0	Singlet.
$\frac{1}{2}$	Doublet.
1	Triplet, etc.



and the multiplicity,  $2S+1$ , is indicated as a superscript preceding the Greek letters; thus

${}^2\Sigma$  corresponds with  $A=0, S=\frac{1}{2}$ , and

${}^3\Delta$  „ „ „  $A=2, S=1$ ,

$S$  being half-integral or integral according as the total number of electrons in the molecule is odd or even. There are two kinds of  $\Sigma$  state in diatomic molecules,  $\Sigma^+$  and  $\Sigma^-$  (in  $\Sigma^-$  states, the wave function changes sign on reflection at a plane through the internuclear line; in  $\Sigma^+$

states, no change of sign occurs). In diatomic molecules with identical atoms all the states belong to odd or even groups, e.g.,  ${}^1\Sigma_g^+$ ,  ${}^3\Pi_u$ , respectively. If the wave function is unaltered on reflection of the co-ordinates at the middle of the line joining the nuclei, the state is even; if it changes sign, the state is odd (see R. de L. Kronig, "Optical Basis of the Theory of Valency," Cambridge, 1935).

The hydrogen molecule has a ground level designated  ${}^1\Sigma_g^+$ , and arises from the union of two

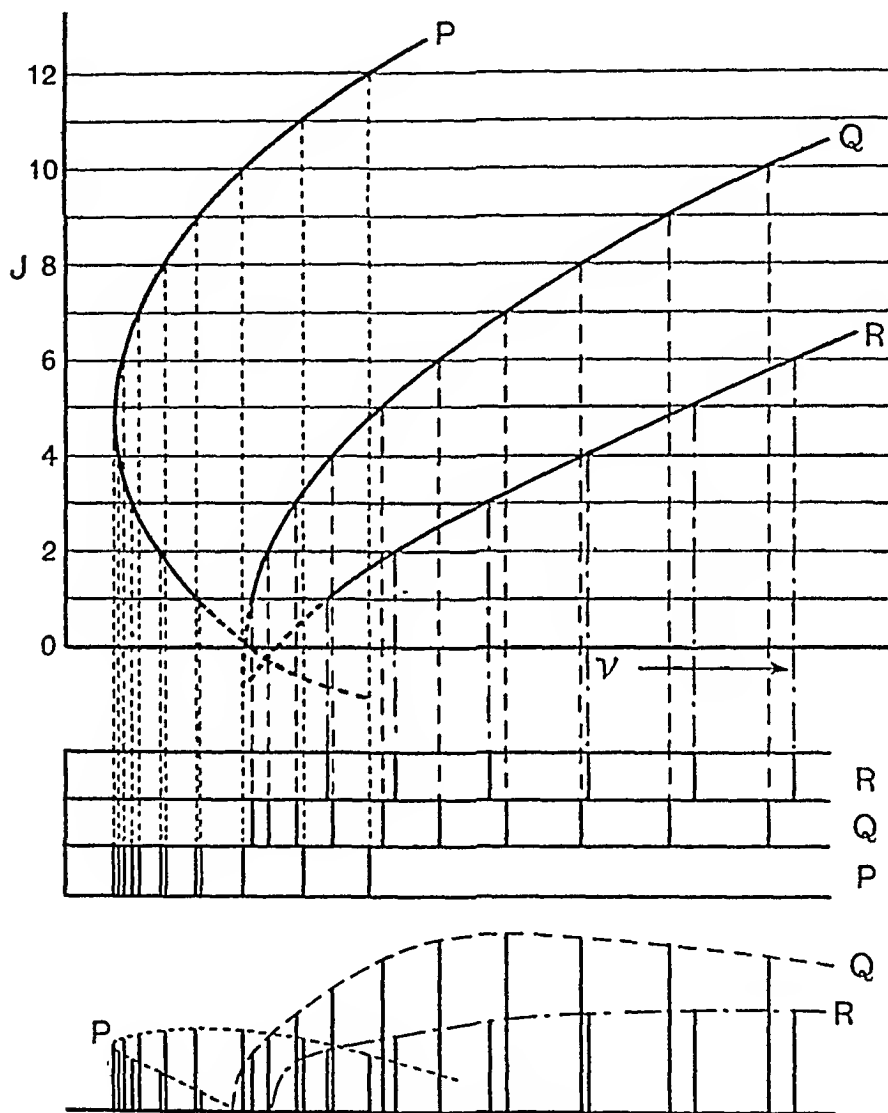


FIG. 4.

atoms in the ground state  $1^2S\frac{1}{2}$  (or  $1S$ ), the two electrons having antiparallel spins. The multiplicity is 1 plus twice the vector sum of the spin ( $1+2\times 0$ ). If the two electrons had parallel spins the multiplicity,  $2(\frac{1}{2}+\frac{1}{2})+1=3$ , would be that of a triplet state  ${}^3\Sigma_u^+$ , which is repulsive, and a stable molecule is not formed. A large number of other levels are known, the upper ones being very much higher than the ground state. Absorption by molecular hydrogen therefore requires the large quanta corresponding with wave-lengths in the vacuum ultra-violet

region. Molecules excited by collisions with electrons, however, emit longer wave-lengths corresponding with smaller changes between one excited level and a lower level. The transition  ${}^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$  affords a special case, in that the  ${}^3\Sigma_u^+$  molecules dissociate into atoms with kinetic energies varying continuously over a wide range. The result is a perfectly continuous spectrum extending from the visible to the far ultra-violet.

Apart from the discrete well-resolved structures so far discussed, diffuse spectra appear



both in absorption and in emission. If no structure can be detected using high dispersion and a narrow slit, the spectrum is said to be *continuous*, and an intermediate type with no recognisable rotational structure is associated with the phenomenon of *predissociation*.

It frequently happens that a more or less abrupt change occurs from a well-resolved to a diffuse spectrum as the wave-length decreases, but much earlier than the short wave-length limit of the progression. The effect arises when discrete levels overlap the continuous state of another electronic level, and is widespread among polyatomic molecules. Thus if a molecule in one of the higher vibration-rotation

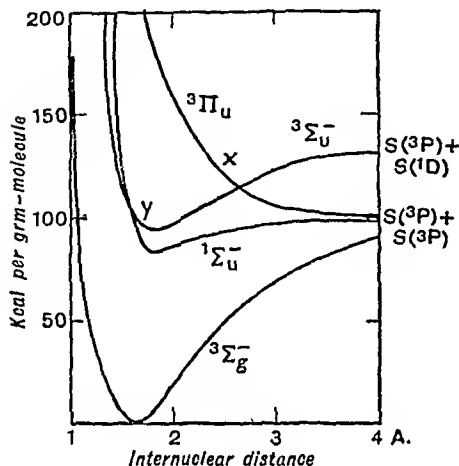


FIG. 5.

The electronic change occurring in the  $S_2$  molecule on absorption is a jump from a  ${}^3\Sigma_g^-$  to a  ${}^3\Sigma_u^-$  level. Absorption in the second, non-pressure-sensitive, diffuse region, causes the molecule to vibrate at energies near the horizontal line through X. The molecule executes a number of vibrations, and then passes through the crossing-point to a repulsive  ${}^3\Pi_u$  level, which at once dissociates into two normal atoms. This behaviour is styled true predissociation. At lower energies of excitation, near Y, the  ${}^3\Sigma_u^-$  curve crosses that for  ${}^1\Sigma_u^-$ . A direct passage between the curves, however, is forbidden by the selection rules. Collisions, by distorting the levels, permit the change and consequent dissociation; hence the pressure-sensitivity of the diffuseness. An effect of this kind is called *induced predissociation*. (Diagram and explanation after E. J. Bowen, "The Chemical Aspects of Light," Oxford, 1942, p. 83.)

levels of an electronic state B exceeds the limit of the vibrational levels of a state A, a radiationless transfer may occur spontaneously. In state A the molecule dissociates before completing a rotation. A number of selection rules must be obeyed (see advanced treatises on molecular spectra, referred to on p. 201d). Rotational fine-structure disappears, but vibrational quanta can still be absorbed. Thus the absorption spectrum of diatomic sulphur vapour is capable of high resolution from 4,100 to 2,799 Å., and from 2,715 to 2,615 Å. Between 2,799 and 2,715 Å. rotational fine-structure persists only at very low pressures; at higher pressures collisions make possible a forbidden transition, resulting

in the diffuse predissociation spectrum. Beyond 2,615 Å. the blurred spectrum is shown even at very low pressures, and true predissociation occurs, i.e., the molecule dissociates after a slight delay of ca.  $10^{-12}$  sec., a time interval between a vibrational and a rotational period. On excitation (absorption) the change is from  ${}^3\Sigma_g^-$  to  ${}^3\Sigma_u^-$ ; the excited vibrating molecule then passes spontaneously to the  ${}^3\Pi_u$  state, which is repulsive, and dissociation occurs instantly into two normal atoms (see Fig. 5).

Dissociation energies may often be evaluated from predissociation limits, but the products of dissociation may carry kinetic energy sufficiently large to make considerable correction necessary (see Kronig, *op. cit.*).

The simple representation of molecular states in terms of  $V/r$  energy curves is replaced in triatomic molecules by an energy surface,  $V(r_1, r_2)$ , for each state. Predissociation is likely for a vibration-rotation level B if its energy surface intersects that of a state A at a place corresponding with the continuum (dissociation); in reality there is an intersection curve replacing the intersection point, and predissociation occurs over a wider spectral range than is usual for the simpler molecules. When there are more than three atoms in a molecule discrete electronic band spectra are unusual, and predissociation is the rule rather than the exception. The dissociation products, moreover, may be atomic or molecular, and are often in states of electronic excitation.

The spectra of the larger molecules are difficult to interpret fully, not only because of the plurality of modes of vibration, but also because of anharmonicity resulting in complex interactions. This together with electronic excitation, leads to a situation which requires either simplifying assumptions or a more empirical approach.

Predissociation spectra are of great importance in understanding photochemical processes (*v. PHOTOCHEMISTRY*).

## EXPERIMENTAL ASPECTS OF BAND SPECTRA.

(a) EMISSION SPECTRA.—Band systems are often observed in flames obtained by simple combustion of gases or liquids, such as hydrocarbons; other spectra may be excited by introducing gases or fine sprays of liquid or solid into hot flames.

The amount of energy available for excitation is, however, not large, and the spectra correspond with transitions between quite low levels (rarely more than 5 electron volts\*), and the lower level is nearly always the ground state. The bands arise from electrically neutral molecules which are most probably chemically unstable; thus although  $N_2$ ,  $O_2$ , and CO molecules are present, they do not show themselves in flame spectra, because the high levels of excitation needed are not reached in the predominantly thermal processes; the radicals CH,  $C_2$ , and OH, however, manifest themselves readily. Thermal excitation involves collisions

\* Subsequently abbreviated to "e.v."

between molecules, one of which may reach a state with a new nuclear distance. This contrasts sharply with excitation by swiftly moving electrons, which exert little effect on the motions of the heavier atoms, so that band systems involving a considerable change in  $r_e$  are not common in discharge tubes or arc sources. The flames of burning hydrocarbons thus show the CH bands at 4,300 and 3,900, the  $C_2$  (Swan) bands and the OH band at 3,064 Å. The Angstrom system of CO shows up in the positive column of an uncondensed discharge with carbon monoxide or dioxide, and the well-known Third Positive bands are equally readily excited. Requiring about 10 e.v., they are absent from flames. The coal-gas Bunsen flame shows the (green)  $C_2$  Swan bands in the green part of the roaring flame, and the CH and OH bands occur in the blue part.

The spectra of metallic oxides are often excited by introducing volatile halides into a flame, but sometimes a lower halide such as  $CaI$  or  $SrBr$  may persist long enough to dominate the observed spectra. Metallic hydrides like  $MgH$  and  $CuH$  exhibit band systems when the finely divided metal is introduced into a hydrogen flame. Cool flames, obtained by slow combustion at temperatures well below the ignition temperature for a normal flame, like those of burning carbon disulphide or ether, are not hot enough for thermal excitation. The spectra of cool flames are due to chemiluminescence, the emitting molecules being excited as a direct result of the combustion processes and not by thermal processes (*v. CHEMILUMINESCENCE*, Vol. III, 22*d*). In the hot flame, carbon disulphide forms  $S_2$  and an oxide of carbon; in the cool flame,  $SO$  and  $CS$  bands are shown. The emitter in the cool flames of ether, acetaldehyde, propionaldehyde, and hexane, is formaldehyde, which is formed in an activated state and displays its fluorescence spectrum. The process is again one of chemiluminescence.

In general, emission spectra are determined by two main factors: (a) the probability of the electronic transition, and (b) the kind and number of collisions which the excited molecule may encounter. The radiative life can be calculated when the absorption spectrum is quantitatively determinable. For absorption the transmitted intensity  $I$  is given by  $I = I_0 e^{-al}$  where  $I_0$  is the incident energy,  $l$  the length of the light path, and  $a$  the absorption coefficient.

For a given band  $\int_0^\infty a \cdot d\nu$  is a measure (usually obtained by graphic integration) of the total absorption.  $N_1$ , the number of molecules per c.c. in the initial state for absorption, can be obtained by using the Boltzmann factor  $e^{-E/kT}$  and the *a priori* probability,  $p_1$ , of the state. If there is no degeneracy this probability, or statistical weight, is unity; if there are two superimposed levels it will be 2, etc. In the simplest case of a transition from state 2 to state 1 the life  $\tau$  of the excited molecule is the reciprocal of the transition probability  $A_{21}$ . This is given by Tolman's expression:

$$A_{21} = (8\pi\nu^2/c^2 N_1)(p_1/p_2) \int_0^\infty a \cdot d\nu.$$

Quantitative spectrophotometric data may be used to determine the oscillator strength  $f$ . If  $N_{abs.}$  stands for the number of *absorbing* molecules per c.c. and  $N_{el.}$  the number of *dispersing* electrons per c.c.,

$$N_{el.}/N_{abs.} = f \left[ N_{el.} = (mc^2/\pi e^2) \int_0^\infty a \cdot d\nu \right].$$

The transition probability  $A_{21}$  is given by

$$A_{21} = (p_1/p_2)(8\pi^2 e^2 \nu_2 / mc) \times f = (p_1/p_2) \nu^2 \times 0.67f.$$

The excited OH radical has  $\tau = 4 \times 10^{-6}$  sec., whereas for excited CN it is about  $1 \times 10^{-8}$  sec., the latter figure being typical for transitions permitted by selection principles.

The period between collisions, derived from the kinetic theory of gases, is about  $1.3 \times 10^{-10}$  sec. for air at N.T.P. In works on molecular spectra the collision life is the average time for an excited molecule to be deactivated by collisions. At low gas-pressures the number of collisions may be  $10^7$  per second, and if the excited molecule has a radiative life of  $10^{-6}$  sec., deactivation by collision may become very efficient. Thus the fact that oxygen inhibits the First Positive band system of nitrogen shows that the excited molecules lose their energy more readily by collisions than by spontaneous emission of light. On the other hand, the long-persistent glow of active nitrogen is an instance of the opposite effect. Experimentally, the collision life is best studied by following the quenching of fluorescence by increasing the pressure or introducing foreign molecules.

The following works are valuable for a fuller study:—

W. Jevons, "Report on Band Spectra of Diatomic Molecules," Physical Society, London, 1932.

G. Herzberg, "Molecular Spectra and Molecular Structure," Prentice-Hall, 1939.

R. de L. Kronig, "The Optical Basis of the Theory of Valency," Cambridge, 1935.

R. W. B. Pearce and A. G. Gaydon, "The Identification of Molecular Spectra," Chapman and Hall, 1941.

A. G. Gaydon, "Spectroscopy and Combustion Theory," Chapman and Hall, 1942.

H. Sponer, "Molekülspektren," 2 Vols., J. Springer, 1935; Sponer and Teller (Rev. Mod. Physics, 1941, 15, 75).

#### (b) SOLUTION SPECTRA.

Notation.—Incident light of intensity  $I\lambda$  is weakened by passage through a small thickness  $l$  of medium in accordance with

$$-dI\lambda = aI\lambda dl \text{ or } -dI\lambda/I\lambda = adl.$$

By integration, putting  $I\lambda = I_0$  for  $l=0$ ,  $\log(I_0/I) = kl$ ; i.e.  $I = I_0 e^{-al}$  (Lambert's Law), indicating that each successive layer absorbs an equal fraction of the light. By replacing  $e$  (natural base) by 10,  $I = I_0 \times 10^{-Kl}$ , and  $K$  is the extinction coefficient of Bunsen and Roscoe, defined as the reciprocal of the thickness ( $l$  cm.) needed to weaken the light to one-tenth of its incident intensity, i.e.,  $\log(I_0/I) = Kl = E$  (extinction). Absorption will then be proportional to the number of molecules in the light path, e.g., a 1-mm. layer of M. solution will exert the same effect as a 1-cm. layer of 0.1 M. solution, or a 10-cm. layer of 0.01 M. solution:

$$I = I_0 \cdot 10^{-\epsilon cl},$$

HEADS OF THE SWAN SYSTEM OF  $C_2$   
(after Jevons).

$\lambda$ .	$\nu$ .	$I$ .	$v' v''$ .	$\lambda$ .	$\nu$ .	$I$ .	$v' v''$ .
6,677.3		1	2, 5	5,501.9		4	3, 4
6,599.2		1	3, 6	5,470.3		2	4, 5
6,533.7		2	4, 7	5,165.2	19,355	10	0, 0
6,480.5		2	5, 8	5,129.3	19,490	6	1, 1
6,442.3		2	6, 9	5,097.7	19,611	1	2, 2
6,191.2	16,147	3	0, 2	4,737.1	21,104	9	1, 0
6,122.1	16,330	4	1, 3	4,715.2	21,202	8	2, 1
6,059.7	16,498	3	2, 4	4,697.6	21,282	7	3, 2
6,004.9		3	3, 5	4,684.8	21,340	4	4, 3
5,958.7		2	4, 6	4,678.6		2	5, 4
5,923.4		1	5, 7	4,668.7		1	6, 5
5,635.5	17,740	8	0, 1	4,382.5	22,812	2	2, 0
5,585.5	17,899	8	1, 2	4,371.4	22,870	4	3, 1
5,540.7	18,043	6	2, 3	4,365.2	22,902	5	4, 2
$v'' =$ 0                      1                      2                      3                      4							
$v' = 0$	19,355	1,615	17,740	1,593	16,147		
	1,749		1,750		1,752		
1	21,104	1,614	19,490	1,591	17,899	1,569	16,330
	1,708		1,712		1,712		1,713
2	22,812	1,610	21,202	1,591	19,611	1,568	18,043
			1,668		1,671		1,673
3			22,870	1,588	21,282		18,171
					1,620		
					22,902	1,562	21,340

The wave-number differences are not quite constant, but the expression

$$\nu = 19,355 + 1,700v' - 20v'^2 - (1,625v'' - 11.5v''^2)$$

reproduces the data with some accuracy.

If the ground state is  $^3\Pi_u$  the  $^3\Pi_g$  state is about  $19,379 \text{ cm.}^{-1}$  higher, and the frequencies  $\omega'$  and  $\omega''$  calculated for infinitesimal amplitude are  $\omega_e'$  1,641.7 and  $1,792.5 \text{ cm.}^{-1}$ , with  $x_e'\omega_e'$  11.7 and  $x_e''\omega_e''$  19.3  $\text{cm.}^{-1}$ . The dissociation energy  $[C(^3P) + C(^3P)]$  is 87 kg.-cal.

The numbers in diagonal rows are *sequences*, e.g., 19,355 (0, 0), 19,490 (1, 1), and 19,611 (2, 2). The more widely spaced numbers in the horizontal or vertical rows form *progressions*, e.g., 19,355 (0, 0), 17,740 (0, 1), and 16,147 (0, 2) ( $v' = 0$  progression). In the Swan system the bands are degraded to the violet and are single-headed. The sequences are quite evident.

where  $c$  is molar concentration,  $l$  is thickness in cm., and  $\epsilon$  is the molecular extinction coefficient. In certain types of work it is more convenient to write

$$I = I_0 e^{-4\pi k l / \lambda} \quad (k = 0.1832\epsilon c \lambda, \lambda \text{ in cm.}).$$

The density  $E$  is equal to  $\epsilon c l$ , and  $E_l^c$  stands for  $\log(I_0/I)$  for an  $l$ -cm. layer of solution of concentration  $c$ . This notation is used to specify actual observations, since most spectrophotometers are graduated on a scale with  $\log(I_0/I)$  ( $E$ ) values of 0.1, 0.2, 0.3, etc. In referring to experiments with products of unknown molecular weight or mixtures,  $c$  may be expressed in percentage (wt./vol.) of solute. Thus if a 0.3-cm. layer of a 0.25% solution transmits one-tenth of the light at  $285 \text{ m}\mu$ .,

$$E_{0.3 \text{ cm.}}^{0.25\%} = 1.0,$$

$$\text{and } E_{1 \text{ cm.}}^{1\%}(285 \text{ m}\mu) = \frac{1.0 \times 1 \times 1}{0.25 \times 0.3} = 13.3.$$

Spectral absorption-curves may be plotted

showing molecular extinction coefficients  $\epsilon$  against  $\lambda$  (in A. or  $\text{m}\mu$ ). It is sometimes more convenient to plot  $\log \epsilon$  against  $\lambda$ . Many workers have used, instead of  $\lambda$ ,  $1/\lambda$  (wave numbers) or  $\nu = c/\lambda$  (frequency) where  $c$  is the velocity of light ( $3 \times 10^{10} \text{ cm. per sec.}$ ).

**Technique.**—(See W. R. Brode, "Chemical Spectroscopy," New York, J. Wiley and Sons, Inc., 1943, Chap. VIII.)

(a) *Visual Determinations.*—Light from a continuous-spectrum source passes through two cells, one containing solvent and the other the solution under investigation. Two images are projected on to the slit of the spectroscopie, and the beams are made parallel by a biprism or some alternative optical device. The solute will weaken the light to an extent varying with the wave-length, and this can be matched by mechanical or other methods of reducing the intensity of the comparison beam. Polarising photometers (Hilger-Nutting, Bausch and Lomb, König-Martens, Hardy) employ two beams polarised in opposite directions and made parallel by a second (analyser) polarising

prism, which on rotation reduces the intensity of the comparison beam by amounts which can be read off on a graduated scale. The accuracy attainable depends upon a variety of conditions, but with newer types may be better than  $\pm 4\%$ . A high-speed sector has been successfully used in the Keuffel-Esser photometer. It depends upon the fact that a rapidly flickering light of high intensity is visually the same as uninterrupted weaker light.

(b) *Objective Determinations.*—The most trustworthy data are obtained by methods involving the use of monochromatic light and the measurement of transmission through the solution and the solvent cells by photo-electric cells. Much depends on the degree of monochromatism, and it is necessary to use a large number of wave-lengths if the solute exerts resolved absorption, but under favourable conditions molecular extinction coefficients can be determined to better than  $\pm 0.1\%$ . The best results are obtained using null methods. For infra-red rays a thermopile can be used instead of a photoelectric cell, whilst for ultra-violet rays quartz photo-electric cells are available. The Hardy recording spectrophotometer (made by the General Electric Company) is almost fully automatic, and although too costly as yet for most workers has justified the labour devoted to it.

The Beckman quartz photoelectric spectrophotometer (Cary and Beckman, *J. Opt. Soc. Amer.* 1941, 31, 682), marketed by the A. H. Thomas Co. of Philadelphia, has proved outstandingly successful to a large number of users. It is a self-contained instrument with a quartz prism serving as a monochromator. There are two easily exchangeable light sources, one a tungsten lamp suitable for the visible and ultra-violet as far as 3,200 Å. and the other a hydrogen tube of convenient size and good performance providing a continuous spectrum for the whole of the "quartz ultra-violet" region. The instrument operates on an electronic circuit and makes use of twin photoelectric cells and a built-in electronic meter for translating photoelectric currents into direct readings of percentage transmission and density. The resolution achieved is adequate for most research and control investigations of solution spectra and with careful use highly reproducible results are obtained; the accuracy in an absolute sense exceeds that obtainable by photographic methods by a factor of from 5 to 10. This fact enables spectrophotometric analyses to be approached in novel ways. The large-scale production of photoelectric spectrophotometers of adequate performance is a war-time development of great significance.

(c) *Photographic Determinations.*—Given a constant light source showing a continuous spectrum, two photographs of the spectrum may be taken using equal exposures in one case with, and in the other case without interposing an absorbing material in the light path. Blackening of the negative will be less for those wave-lengths at which the material absorbs. The darkening of the photographic negative can be measured accurately in terms of transmission through the plate, recorded by a thermopile and galvanometer or by photoelectric methods.

One successful technique consists in taking several spectrograms of the source without varying the exposure, but in each case reducing the intensity by a known amount by some mechanical device (screens, grey wedges, diaphragms, etc.). A registering microphotometer traces the variations in blackening both for the control spectra and the solution spectrum, the wave-lengths of intersection (match points) providing the data for spectral absorption-curves.

Alternatively, match points may be read off visually from pairs of photographs, as in the plates obtained with rotating sector photometers and the new "Spekker" photometer.

The adjustment of spectrophotometric apparatus may be checked by determining the absorption of an easily accessible substance which has been thoroughly studied, e.g., 0.003*N.* potassium chromate in 0.05*N.* potassium hydroxide solution, data for which are as follows:

$\lambda_{\max.}$ (Å.)	$\epsilon_{\max.}$	$\lambda_{\min.}$ (Å.)	$\epsilon_{\min.}$
2,725	3,660	2,290	752
3,715	4,830	3,125	203

**Inorganic Compounds.**—Solutions of inorganic substances are in a very large number of cases transparent in the region 2,000–8,000 Å. Thus the ions  $\text{Na}^+$ ,  $\text{K}^+$ , etc., and  $\text{NH}_4^+$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ , etc., owe their lack of selective absorption to completed outer shells of electrons. The ions  $\text{ClO}_4^-$  and  $\text{SO}_4^{--}$  likewise are transparent. The  $\text{NO}_3^-$  ion shows a weak band,  $\lambda_{\max.}$  3,020 Å.,  $\epsilon_{\max.}$  6.4, due to a forbidden transition which only occurs when coupled with certain vibrational frequencies, although intermolecular Stark effects in solution (modifications brought about by strong electric fields) smooth out all evidence of structure. At  $-250^\circ$  crystalline nitrates exhibit vibrational frequencies (350 and 750  $\text{cm}^{-1}$ ), but the location of the absorption depends on interionic forces:

Crystal.	$\text{KNO}_3$	$\text{NaNO}_3$	$\text{Ba}(\text{NO}_3)_2$	
$\lambda_{\max.}$ (Å.)	3,040	2,915	2,775	(at room temperature).
	3,070	2,870	2,725	(at $-250^\circ$ ).

If changes in concentration leave the molecular extinction coefficient unchanged, Beer's law is obeyed. Departures from the law indicate some significant change in the system, e.g.:

#### Sulphur dioxide in water.

	$\lambda_{\max.}$ (Å.)	$\log \epsilon_{\max.}$
0.004 M.	2,750	1.82
0.04 M.	2,750	2.2
0.1 M.	2,750	2.4
0.4 M.	2,750	2.2

Sulphur dioxide in hexane  
(Beer's law obeyed. Solute not solvated).

$\lambda_{\max.}$ (Å.)	$\log \epsilon_{\max.}$
2,900	2.4

The following equilibria obtain:



and the solvated sulphur dioxide is the only selectively absorbing constituent.

Departures from Beer's law in concentrated nitric acid indicate formation of ion pairs ( $\lambda_{\max}$ , 2,650 Å. in 15N-HNO<sub>3</sub> or 0.15N-HNO<sub>3</sub> in 9N-HClO<sub>4</sub>), but nitric acid in pure hexane merely shows an inflexion near 2,800 Å. similar to that shown by ethyl nitrate.

Solutions of permanganates and also crystals at low temperatures exhibit electronic band-spectra in the visible and in the ultra-violet, characterised by a number of equidistant bands, the frequency separations of which correspond with totally symmetrical vibrations (expansion and contraction of the MnO<sub>4</sub><sup>-</sup> tetrahedron). The selective absorption is due to the fact that the ion possesses an incomplete shell of electrons well shielded by valency electrons. The tetrahedral ions of most of the transition elements show essentially similar spectra, in marked contrast to the transparent ClO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> ions. The rare-earth ions also owe their highly selective absorption to shielded, incomplete electronic shells, but new complications arise in certain cases. Thus neodymium

chloride hexahydrate crystals at -250° exhibit electronic transitions coupled with internal vibration frequencies of the molecules, as well as various modes of lattice vibration. Neodymium chloride and bromate exhibit structure (under these conditions) indicative of vibration frequencies 1,640-1,650 cm.<sup>-1</sup> with ordinary water of crystallisation, and 1,199-1,238 and 1,431-1,481 cm.<sup>-1</sup> with deuterium oxide of crystallisation. From other data the values of these inner vibrations are 1,615 cm.<sup>-1</sup> or 1,220 and 1,460 cm.<sup>-1</sup>, respectively. With europium salts the spectra are so sharp that inner vibration frequencies can be determined at room temperatures.

**Absorption Spectra of Organic Compounds.**—Methane and ethane show selective absorption in the vacuum ultra-violet region only (1,200-1,300 Å.), but replacement of hydrogen by alkyl groups brings about displacements towards longer wave-lengths (cf. *n*-hexane, 1,530 Å.). Ethylene absorbs in the region 1,300-1,750 Å., showing a number of

TABLE I.—ABSORPTION DATA FOR TYPICAL COMPOUNDS CONTAINING ETHYLENIC LINKINGS.

	$\lambda_{\max.}, m\mu.$	$\epsilon_{\max.}$	Solvent.
CH <sub>2</sub> =CH <sub>2</sub> . . . . .	ca. 180	ca. 10,000	
CH <sub>2</sub> =CH-CH=CH <sub>2</sub> . . . . .	217	21,000	Hexane
CH <sub>2</sub> =CMe-CMe=CH <sub>2</sub> . . . . .	224	20,000	Hexane
CH <sub>2</sub> =CH-CH <sub>2</sub> -OH . . . . .	<195	ca. 10,000	Hexane
CH <sub>3</sub> -[CH=CH] <sub>2</sub> -CH <sub>2</sub> -OH . . . . .	ca. 232		Alcohol
CH <sub>3</sub> -[CH=CH] <sub>3</sub> -CH <sub>2</sub> -OH . . . . .	268	53,100	Alcohol
CH <sub>3</sub> -[CH=CH] <sub>4</sub> -CH <sub>3</sub> . . . . .	274	4,200	Hexane
	284	8,400	
	296	12,000	
	320	12,000	
CH <sub>3</sub> -[CH=CH] <sub>4</sub> -CH <sub>2</sub> -OH . . . . .	310	44,700	Alcohol
	330	5,800	
CH <sub>3</sub> -[CH=CH] <sub>6</sub> -CH <sub>3</sub> . . . . .	340	10,600	Chloroform
	360	16,000	
	372	11,400	

sharp bands, the frequencies of which fit into a Rydberg formula :

$$C_2H_4: \nu_0(n) = 84,750 - R/(n+0.91)^2; \\ n=2, 3, 4, \text{ etc.}$$

$$C_2D_4: \nu_0(n) = 84,850 - R/(n+0.92)^2; \\ n=2, 3, 4, \text{ etc.}$$

and converge to an ionisation potential of 10.45 v.

Wave-mechanical theory distinguishes between localised electron-pairs responsible for directed valency ( $\sigma$  electrons) and "mobile" electrons ( $\pi$ ) which cannot be paired according to their spins in a unique way to fit an ordinary structure; the latter are not strictly localised and in planar molecules are antisymmetrical to the plane of the C-C links. The characteristic absorption of ethylene is due to the excitation and removal of a  $\pi$  electron from the double bond, and the greater transparency of the saturated hydrocarbons reflects the higher

frequencies necessary for ionisation by breaking [ $\sigma$ ]<sup>2</sup> C-C or C-H links. Ethylene exhibits vibrational structure [ $C_2H_4$ ,  $\Delta$ (cm.<sup>-1</sup>)=1,370;  $C_2D_4$ , 1,290] corresponding with the totally symmetrical valency frequency of the double bond. Butadiene exhibits resonance between conjugated double bonds. A progression of four diffuse bands occurs near 2,170 Å. ( $\Delta$  1,440 cm.<sup>-1</sup>). Other electronic states give rise to absorption at higher frequencies, and below 1,520 Å. vibrationless transitions lead to ionisation (9.02 v.).

$$\nu_0(n) = 73,115 - R/(n+0.90)^2; \quad n=2, 3, 4, \text{ etc.} \\ = 73,006 - R/(n+0.50)^2; \quad n=3, 4, 5, \text{ etc.}$$

The ionisation potential is further diminished with alkyl substitution.

The ethylenic linkage constitutes the simplest chromophore or absorbing entity in the study of organic compounds in solution, since all fully saturated hydrocarbons (e.g., cholestane, pregnane, decalin) are transparent to radiations of wave-length >200  $m\mu$ .

The following generalisations facilitate the interpretation of results for organic compounds:

1. Certain groupings,  $C_nH_{2n+1}$ , OH, etc., are transparent in the region 200–800  $m\mu$ .
2. Functional or chromophoric groupings ( $-\text{CH}=\text{CH}-$ ,  $>\text{C}=\text{O}$ ,  $-\text{N}=\text{N}-$ ,  $\text{C}_6\text{H}_5-$ ,  $\text{C}_{10}\text{H}_7-$ ,  $-\text{NO}$ , etc.) give rise to selective absorption. This may undergo displacement in the direction of longer wave-lengths, according to the complexity of the molecule containing the simple chromophore.
3. Simple chromophores differ in respect of intensity of absorption (probability of a given electronic transition); thus  $>\text{C}=\text{O}$  in the middle ultra-violet gives rise to much weaker absorption than in the region 200  $m\mu$ , where both  $>\text{C}=\text{O}$  and  $-\text{CH}=\text{CH}-$  show intense absorption.

4. In a molecule containing two simple chromophores, the observed absorption is simply additive, provided that the chromophores are insulated, i.e., separated by one or more  $\text{CH}_2$  groups.
5. When two chromophores are conjugated they may exert considerable mutual effects, or be merged into a complex chromophore.
6. Certain groupings (e.g.,  $-\text{COOH}$ ), which are not in themselves powerful chromophores, may induce considerable displacements of selective absorption caused by other chromophores from which they are not insulated.
7. In many large molecules separate portions can sometimes function independently, and the observed absorption spectrum may be made up of "partials."

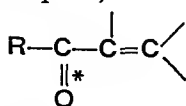
The above generalisations provide little more than an introduction, but examples will illustrate their utility.

TABLE II.—ABSORPTION DATA FOR KETONES.

	$\lambda_{\text{max.}}, m\mu.$	$\epsilon_{\text{max.}}$	Remarks.
$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ . . . . .	279	15	The whole range of aliphatic ketones shows similarly feeble but selective absorption in this region.
$(\text{CH}_3)_3\text{C}\cdot\text{CO}\cdot\text{C}(\text{CH}_3)_3$ . . . . .	296	20	
$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ . . . . .	327	40	CO band displaced from 210 $m\mu$ .
	220	12,600	$-\text{CH}=\text{CH}-$ band displaced from 185 $m\mu$ .
$\text{CH}_3\cdot[\text{CH}=\text{CH}]_2\cdot\text{CO}\cdot\text{CH}_3$ . . . . .	264	20,800	$-\text{CH}=\text{CH}-$ band displaced from 220 $m\mu$ .
$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CO}\cdot\text{CH}=\text{C}(\text{CH}_3)_2$ . . . . .	375	80	CO band displaced.
	295	23,500	Ethylenic absorption influenced by conjugated groups.
$\text{CH}_3\cdot[\text{CH}=\text{CH}]_2\cdot\text{CHO}$ . . . . .	270	26,500	$-\text{CH}=\text{CH}-$ band displaced.

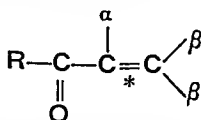
It is convenient to consider the absorption of  $\alpha\beta$ -unsaturated ketones as made up of the summation of:

(a) ketonic absorption,



the \* indicating the site of the process ( $\lambda_{\text{max.}} > 275 m\mu$ ,  $\epsilon_{\text{max.}} < 100$ ), and

(b) ethylenic absorption,



of high intensity, the act of absorption being connected primarily with a mobile electron, and the location depending on the substituents  $\alpha\beta$ .

It has been found that the displacement of the ethylenic absorption is of diagnostic value.

Substitution.	$\lambda_{\text{max.}}, m\mu.$	No. of Examples.
$\beta\beta=\text{H}, \text{H}$ . . . . .	218	
Mono, $\alpha$ and $\beta$ . . . . .	$225 \pm 5$	6
Di, $\alpha\beta$ or $\beta\beta$ . . . . .	$239 \pm 5$	36
Tri, $\alpha\beta\beta$ . . . . .	$254 \pm 5$	9

The spectra of polyenes generally show that progressive displacements of absorption maxima in the direction of longer wave-lengths, and step-wise increments in intensity of absorption, accompany increasing number of conjugated double bonds (see Table I). The system of  $(-\text{CH}=\text{CH}-)_n$  oscillators can be regarded as a single oscillator with the same coefficient of restoring force,  $k$ , and mass proportional to  $n$ .

The energy levels for an oscillator of mass  $nm$  are given by :

$$W_v = (v + \frac{1}{2})h\nu_0 \\ (v=0 \text{ to } v=1) \text{ and} \\ 2\pi\nu_0 = \sqrt{(k/nm)},$$

where  $\nu_0$  is the frequency of the first absorption band, and  $\lambda_0 = 2\pi c / \sqrt{(k/nm)}$  or  $\lambda_0^2 = 4\pi^2 c^2 nm / k$ , i.e.,  $\lambda_0^2 = k'n$ . On plotting  $\lambda_0^2$  against  $n$  a straight line may be obtained, e.g., with the diphenyl polyenes, for which it cuts the  $n$  axis at  $-4.7$ , so that in this series each phenyl group is equivalent to 2.35 double bonds.

As in simple molecules, higher vibrational levels involve increasing anharmonicity, and there is some evidence that with  $v=2$ , second-order bands may be observed, e.g., the 270  $m\mu$ . absorption often seen in carotenoids. In the  $p$ -polyphenyls the internuclear link is of a type intermediate between a single and a double bond, and the molecules are, to some extent at least, resonating as a whole and behaving as linear oscillators. The analogous series of  $m$ -polyphenyls, on the other hand, all show absorption near 253  $m\mu$ ., with molecular extinction coefficients consistent with a "semi-diphenyl" chromophore functioning additively.

The spectra of polycyclic hydrocarbons (at least in so far as the location of the first absorption region is concerned) may be predicted by the methods of wave mechanics. In order to calculate C-C distances and the location on the wave-length scale of absorption, one experimental quantity,  $\alpha$  or  $J$ , is needed. This is calculated from heats of hydrogenation and is given by Sklar (J. Chem. Physics, 1937, 5, 669) as 1.92 e.v. (44 kg.-cal. per g.-mol.). Benzene is treated as a six-electron system with spin degeneracy only, and the single exchange integral between adjacent carbon atoms is  $\alpha$ . The data for a number of polycyclic hydrocarbons being taken into account, a better figure for  $\alpha$  is 2.11 e.v., but the work represents only a first approximation.

Benzene may be used as an example of the relatively small number of organic compounds yielding well resolved spectra. It shows

- banded emission produced by a Tesla coil discharge through benzene vapour. The spectrum consists of evenly spaced groups of bands degraded to the red, and resembling the sequences shown in the spectra of diatomic molecules. At least 25 heads may be recognised in the region 2,600-2,904 Å.
- a somewhat similar spectrum in absorption, given by benzene vapour, liquid benzene, or solutions. The bands are evenly spaced and degraded to the red. In solutions they are shifted towards the red and less sharp, except at very low temperatures. They extend from 2,275 to 2,680 Å. and show quite low molecular extinction coefficients.
- a fluorescence spectrum (benzene in solution), in essentials similar to the emission spectrum, and covering the range 2,650 to 3,005 Å.
- other more intense bands in the more distant ultra-violet.

### Spectra of Benzene.

(Cf. Sponer and Teller, Rev. Mod. Phys. 1941 13, 140.)

Absorption and fluorescence bands 2,200-2,800 Å.

$^1A_{1g} \leftrightarrow ^1B_{2u}$ . 0, 0 band (calculated) at 38,089  $cm^{-1}$ .

$^1A_{1g}$ =ground state. Transition is forbidden according to selection rules, but becomes allowed by excitation of vibrations (type  $\epsilon_g^+$ ).

Series revealed by analysis :

Series.

A  $\nu = 38,089 + 520 + v_1' \times 923 - v_1'' \times 992 + v_2' \times 2,565 - v_3 \times (400-240)$ .

B  $\nu = 38,089 - 606.4 + v_1' \times 923 - v_1'' \times 992 + v_2' \times 2,565 - v_3 \times 160$ .

C  $\nu = 38,089 + 520 \times 2 - 606.4 + v_1' \times 923 + v_2' \times 2,565 - v_3 \times 160$ .

D  $\nu = 38,089 + 520 - 606.4 \times 2 + v_1' \times 923 - v_3 \times 160$ .

E  $\nu = 38,089 + 1,480 + v_1' \times 923$ .

F  $\nu = 38,089 - 1,596 - v_3 \times 160$ .

G  $\nu = 38,089 + 520 + 249 \times 2 + v_1' \times 923 - v_3 \times 160$ .

H  $\nu = 38,089 - v_3 \times 160$ .

with  $v_1' = 0, 1, 2 \dots$ ;  $v_1'' = 0, 1, 2$ ;  $v_2' = 0, 1$ ;  $v_3 = 0, 1 \dots$

Ring vibrations C-C  $\omega'' 992 \omega' 923 (a_{1g})$ .  
606.4, 520, 1,480,  
1,596 ( $\epsilon_g^+$ ).  
400, 240 ( $\epsilon_u^+$ ).

Valence vibration C-H. 2,565  $cm^{-1}$ .

Absorption bands . . 1,850-2,050 Å.

$^1A_{1g} \rightarrow ^1B_{1u}$ .

Transition forbidden but becomes allowed by excitation of type  $\epsilon_g^+$  vibrations. Bands much stronger because of proximity to allowed system at 1,770 Å. Diffuse bands, 965 and 160  $cm^{-1}$  progressions.

Absorption bands 1,650-1,850 Å.  $^1A_{1g} \rightarrow ^1E_g^-$  very intense sharp bands, also 1,360-1,600 Å.  $^1A_{1g} \leftarrow ^1E_u^-$  absorption bands forming a Rydberg series.

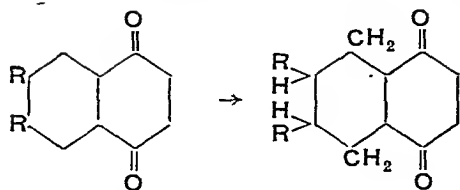
(See Sponer and Teller, *l.c.*, for wave-mechanical treatment and notation.)

Benzene affords a link between the kind of data obtained with diatomic molecules and those characteristic of larger organic molecules. Polyatomic molecules show a great variety of vibrational frequencies, the anharmonicity of which is often marked, and a full analysis of vibrational and rotational structure is often quite impossible. The molecules, moreover, may exhibit several possibilities of dissociation, and may possess numerous excited states, the instability of which results in continuous or diffuse spectra.

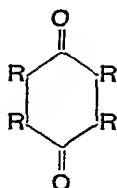
Many workers are exploring the subject, and an important body of knowledge on the electronic structures of polyatomic molecules is being accumulated. This field is difficult to summarise, largely because much of the work is tentative and involves an elaborate apparatus of notation and a specialised mathematical approach.

Almost independently of this branch of





or chromophorically

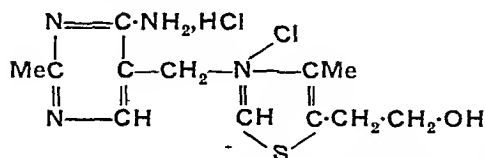


The substituted 1:4-naphthaquinones therefore show spectra accounted for by a simple summation of (a) and (b).

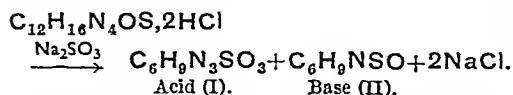
(a)		$\lambda_{\max.} (\text{\AA}).$	$\log \epsilon_{\max.}$
		2,430	4.02
		2,495	4.025
		3,290	3.63

(b)		$\lambda_{\max.} (\text{\AA}).$	$\log \epsilon_{\max.}$
		2,600	4.2
		2,700	4.2

The case of aneurin (vitamin- $B_1$ , see Vol. I, 583b) is of special interest.



By the action of sulphite at room temperature a quantitative cleavage takes place:



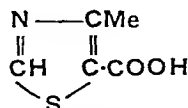
The basic fragment reacts with hydrochloric acid to give  $\text{C}_6\text{H}_8\text{NSCl}$  and water, without appreciable alteration of the absorption spectrum, suggesting replacement of OH on a side chain by Cl. The probability that the sulphur formed part of a ring led to a comparison with thiazoles:

	$\lambda_{\max.} (\text{\AA}).$	$\epsilon_{\max.}$
Hydrochloride of II . . . . .	2,520	4,200
4-Methylthiazole hydrochloride . . . . .	2,510	4,000
2:4-Dimethylthiazole hydrochloride . . . . .	2,530	4,500
2-Hydroxy-4-methylthiazole hydrochloride . . . . .	2,480	4,000

This led to the study of quaternary salts:

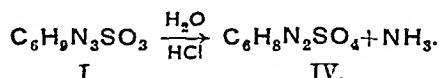
	$\lambda_{\max.} (\text{\AA}).$	$\epsilon_{\max.}$
Methiodide of II . . . . .	2,270	12,500
4-Methylthiazole ethiodide : : . . . . .	2,270	13,200

Synthesis of



gave a product identical with that obtained from (II) by oxidation with nitric acid.

The amino sulphonic acid (I) splits off ammonia to yield an oxysulphonic acid.



This recalls the replacement of  $\text{NH}_2$  by OH in the 2-amino- and 6-amino-pyrimidines:

	$\lambda_{\max.} (\text{\AA}).$	$\epsilon_{\max.}$
Amino-sulphonic acid I . . . . .	2460	10,000
	2680	7,000
Oxysulphonic acid IV . . . . .	2290	5,900
	2750	5,800
2:4-Dimethyl-6-aminopyrimidine . . . . .	2410	9,100
	2600	7,200
2:4-Dimethyl-6-oxypyrimidine . . . . .	2280	6,200
	2580	5,300
4:6-Dimethyl-2-aminopyrimidine . . . . .	2270	10,000
	2870	4,100
4:6-Dimethyl-2-oxypyrimidine . . . . .	2150	9,100
	2960	5,900

The change in absorption when  $\text{NH}_2$  in position 6 is replaced by OH is reproduced so closely that the presence of a pyrimidine ring with a 6-amino substituent was rendered almost certain at an early stage in the work. A cleavage product of aneurin, obtained by treatment with liquid ammonia, contained two  $\text{NH}_2$  groups, and further comparison with synthetic products showed:

	$\lambda_{\max.} (\text{\AA}).$	$\epsilon_{\max.}$
Liquid ammonia cleavage product . . . . .	2,340	6,500
	2,680	5,250
2:5-Dimethyl-6-aminopyrimidine . . . . .	2,350	7,200
	2,680	6,700
4:5-Dimethyl-2:6-aminopyrimidine . . . . .	2,750	6,250
5-Ethyl-4:4-diaminopyrimidine . . . . .	2,680	7,400
4-Methyl-5:6-diaminopyrimidine . . . . .	2,920	10,800

The cleavage product treated with sodium in liquid ammonia gave, in fact, 2:5-dimethyl-6-aminopyrimidine, indicating a methylene bridge between the thiazole and pyrimidine portions in



aneurin. The choice between the two methyls rested upon proof that a synthetic sulphonic acid was identical with one derived from aneurin. This proof depended upon the identity in absorption over a long range of wave-lengths of saturated alcoholic solutions of (a) the synthetic acid, (b) the "natural" sulphonic acid, and (c) both acids. This method provides a very stringent test of identity, and is applicable to many substances which do not melt without decomposition.

A quite different approach to molecular spectra may be illustrated by the work of Warburg and his school on the photochemical determination of the absorption spectrum of the respiratory enzyme (see Kubowitz and Haas, *Biochem. Z.* 1932, 255, 247). The method depends upon the decomposition, by means of monochromatic irradiation, of the carbon-monoxide addition compound. Fifteen convenient wave-lengths between 2,500 and 6,000 Å. being used, the respiration of acetic bacteria or of yeast cells was reduced to 30% of its initial value by carbon monoxide and restored to 60% by irradiation. The absorption spectrum was calculated from the intensities, at the different wave-lengths, needed to effect such an increase.

The distribution  $V = n/(1-n)$  is given when  $n$  is the residual activity, and  $1-n$  that lost by carbon-monoxide poisoning. On irradiation the dark value  $n_d$  is increased to  $n_l$ , the light value if the intensity is  $i$

$$V_d = n_d/(1-n_d) \text{ and } V_l = n_l/(1-n_l),$$

so that

$$\Delta V = n_l/(1-n_l) - n_d/(1-n_d),$$

and the light sensitivity  $L$  is

$$L = (\Delta V/i)/V_d \\ = \{n_l/(1-n_l) - n_d/(1-n_d)\} / \{n_d/(1-n_d)\},$$

the ratio  $\text{CO}/\text{O}_2$  being constant.

If  $N_0 h\nu$  is one molecular quantum, and  $z_d$  the decomposition constant of the dark reaction for the enzyme-CO compound, and  $\beta$  is the light absorption coefficient,

$$L = (1/N_0 h\nu)(\beta/z_d).$$

For two frequencies  $\nu_1$  and  $\nu_2$

$$\beta_1/\beta_2 = (L_1/L_2)(\lambda_2/\lambda_1).$$

A reference line is chosen to obtain relative  $\beta$  values, the 4,360-Å. mercury line being convenient. All the data are then expressed in terms of:

$$\beta_\lambda/\beta_{\lambda_0} = (L_\lambda/L_{\lambda_0})(\lambda_0/\lambda),$$

and the shape of the absorption curve is shown by plotting  $\beta_\lambda/\beta_{4360}$  against  $\lambda$ .

The following works provide fuller information:

G. Scheibe and W. Frömel, "Molekülspektren von Lösungen und Flüssigkeiten," Eucken-Wolf, Hand- und Jahrbuch der Chemischen Physik, Band IX, Abschnitt III-IV, 1937.

H. Mohler, "Lösungsspektren," G. Fischer, Jenn, 1937.

R. A. Morton, "Absorption Spectra of Vitamins, Hormones, and Co-enzymes," A. Hilger, 1942.

R. A. M.

## MOLECULAR WEIGHT DETERMINATION.

**Introduction.**—Physical methods for the determination of molecular weights have engaged attention for more than a century, and the literature on the subject covers a wide range. In this necessarily short article it is proposed to summarise the main types of method which are used; some of these are highly specialised, but are included either because they provide results of particular scientific value, or are suited to special circumstances, such, for example, as the availability of a substance in very minute amount. Main attention will be given to procedures which are generally available in ordinary chemical practice, and mention will be made of alternative micro-methods, which often offer advantages quite apart from economy of material.

The determinations are classified according as the substance under investigation is (I) in the gaseous or vapour state, (II) in the liquid state, (III) in solution, or (IV) in the solid state.

### I. GAS AND VAPOUR METHODS.

**1. Gas Densities.**—Gas-density methods are of importance because they are capable of providing molecular and atomic weights of the highest order of accuracy, and, indeed, are partly responsible for establishing the values of the atomic weights of carbon and nitrogen at present accepted. There are two main experimental modifications; the methods of limiting densities and limiting pressures.

The first of these depends on precise measurements of pressure, volume, and weight of gas contained in a glass bulb; alternatively, in the volumeter method, the vessel used for the pressure and volume measurements is not used for weighing the gas, but instead this is accomplished in a much smaller vessel containing materials from which the gas can be generated, or on which it can be adsorbed or condensed (e.g., oxygen from potassium permanganate, hydrogen from palladium hydride, condensable gases on charcoal cooled in liquid air). In either case great refinement of technique is necessary; all glass vessels are weighed against similar counterpoises, and corrections must be applied for the adsorption of gases on glass surfaces and for the alteration of the volume of vessels on evacuation. It is also essential to allow for the deviations shown by gases from the ideal-gas laws, and this involves density determinations at different pressures so that extrapolation to zero pressure, or zero density, can be carried out. For this purpose, Borthelot's equation is used, i.e.,  $PV = P_0 V_0 (1 - AP)$  where  $P_0 V_0$  is the value of the product  $PV$  at zero pressure, and  $A$  is the "compressibility" of the gas. This assumes strict linearity of the  $PV$  isotherms over the range of pressures used (below 1 atm.), and it has been shown that for gases not more easily liquefiable than carbon dioxide, this assumption can lead only to errors not greater than a few parts per 100,000. Even for gases as easily liquefied as hydrogen chloride, the error involved is very small and can be reduced by use of a non-linear extrapolation equation, but this is seldom necessary. The modern exponent of this work,

Moles, uses the relationship  $M=32.000L_0/L_0'$ , where  $M$  is the molecular weight of the gas under investigation,  $L_0$  is the value of  $\rho/P$  at zero pressure for the gas,  $L_0'$  the corresponding value for oxygen, and  $\rho$  is the density in g. per l. at pressure  $P$  and  $0^\circ\text{C}$ . In every case the density of oxygen is redetermined in the same apparatus and under identical conditions as those used for the gas under investigation; this provides a check on the absolute accuracy of the determination, since the normal density of oxygen is known with very great accuracy to be 1.42893 g. per l.

(mean of 132 measurements by five different authors since 1920). For critical accounts of gas-density methods, see W. Ramsay and M. W. Travers, "The Experimental Study of Gases," London, 1901; "Les Determinations physico-chimiques des Poids moleculaire et atomique des Gaz," Institut Internationale de Cooperation Intellectuelle, Paris, 1938. The volumeter apparatus used by Moles and co-workers is shown diagrammatically in Fig. 1.

The method of limiting pressures depends on the buoyancy microbalance, first applied to the

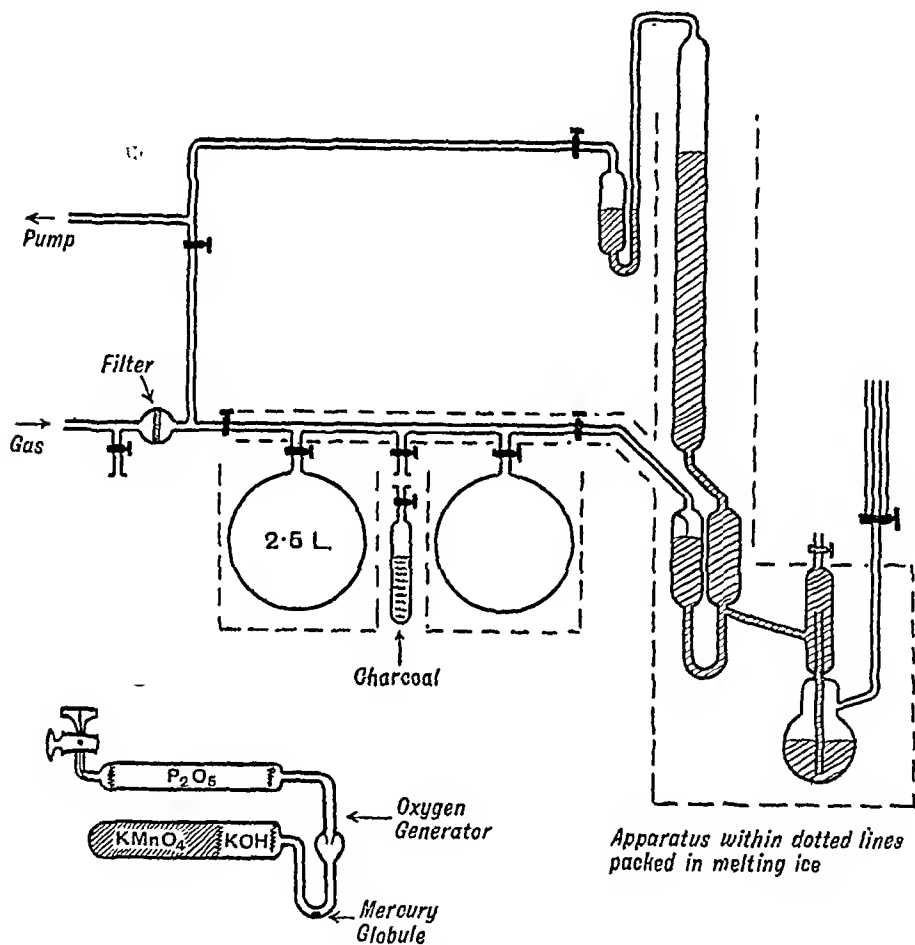


FIG. 1.

determination of gas densities by Steele and Grant (Proc. Roy. Soc. 1909, A, 82, 580). In principle, it consists of a balance of fused silica or Pyrex glass, carrying on one side of the beam a closed bulb greatly exceeding in volume the counterpoise on the other side of the beam. The position of equilibrium of the beam therefore depends on the buoyancy effect of the medium in which it is suspended; the bulb will suffer an effective loss in weight equal to the weight of gas which it displaces. Since the bulb is of fixed volume, the position of the balance beam will be defined by the density of the surrounding gaseous medium. The instrument therefore

serves as a very accurate means of comparing the densities of gases and, if one of these is oxygen, of determining molecular and atomic weights. In practice, the pressures at which the two gases have the same density  $\rho=M/V$ , are determined. Applying the Berthelot equation to one molecule of gas, since  $P_0V_0=RT$ ,  $P=\rho RT(1-AP)/M$  and hence, for the comparison,

$$P/P'=32.000(1-AP)/M(1-A'P'),$$

where  $M$ ,  $A$ , and  $P$  represent the molecular weight, compressibility, and pressure, respectively, of the gas under investigation, and

32-000,  $A'$ , and  $P'$  are the corresponding quantities for oxygen. The ratio  $P'/P$  is determined for a number of different densities and is extrapolated to zero pressure, when  $M=32\cdot000/P$ . The method has the advantage that it can be readily reduced to the micro-scale; the bulb of the balance can be as small as 2 ml., although a volume of 20 ml. is more suitable under normal conditions. It has therefore been used for the determination of the atomic weights of rare gases: radon (Gray and Ramsay, *ibid.* 1910, A, 84, 536), neon (Aston, *ibid.* 1913, A, 89, 440), xenon (Whytlaw-Gray, Cawood, and Patterson, *ibid.* 1931, A, 134, 7), and helium (Taylor, *Physical Rev.* 1917, [ii], 10, 653). The method is attended by certain

peculiar difficulties and, if the apparatus is small, adsorption effects are particularly important. Correction for adsorption of the gas on the balance bulb is usually compensated by furnishing the counterpoise of the balance with a surface, in the form of either a flat plate or an open bulb, equal in area to the surface of the closed buoyancy bulb. In this way, with very careful matching of surface area on each side of the balance beam, the effect of adsorption is automatically cancelled out. A correction must be applied (the Rayleigh correction) for the compressibility of the bulk, and also, when it is rigidly attached to the balance beam, for a resultant lateral shift in the centre of gravity owing to its change in volume with variation of pressure. Quartz-fibre torsion suspension is usually used for the balance beam, although quartz knife-edge or even point suspensions have been successfully used. Since it is necessary to determine pressure ratios at different densities, the load on the counterpoise side of the balance beam must be adjustable. Riders can be used for this purpose, but Stock has developed an electro-

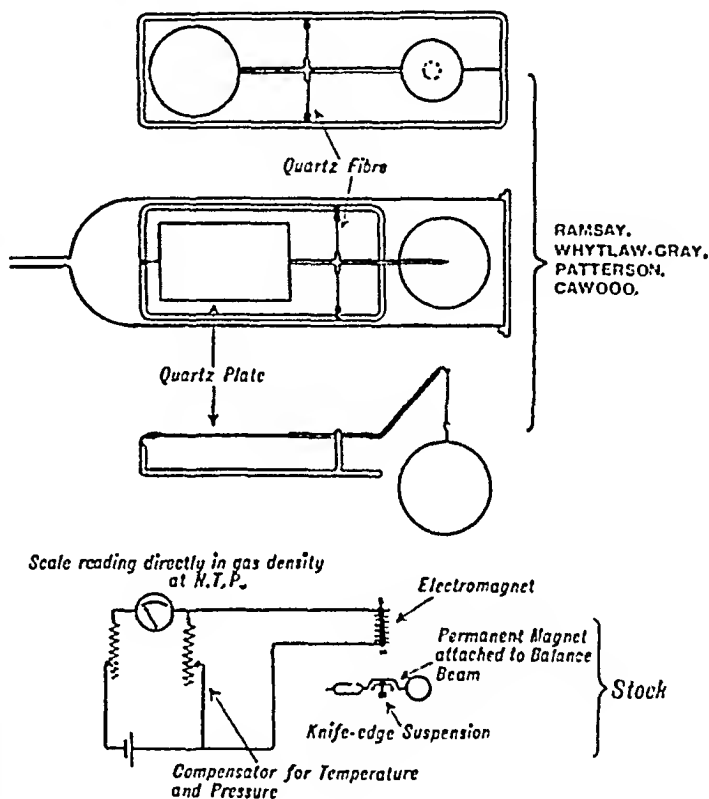


FIG. 2.

magnet incorporated in the construction of the balance beam is influenced by an accurately measured current in an external electromagnetic circuit (A. Stock, *Z. physikal. Chem.* 1928, 139, 47; "The Hydrides of Boron and Silicon," Cornell Univ. Press, 1933, Chap. XXX; Lehrer and Kuss, *Z. physikal. Chem.* 1933, 163, 73). A comprehensive review of construction and performance is given by Stock and Ritter, *ibid.* 1926, 119, 333, and some of the main types are illustrated diagrammatically in Fig. 2.

The method of correction of the normal densities of gases (*i.e.*, densities at 0°C. and 760 mm. pressure) for deviations from ideal behaviour by means of independently determined compressibilities has not been extensively used in accurate molecular weight determinations although the objections to this procedure seem to have been over-accentuated. The

method suggested by Guye, *J. Chim. phys.* 1905, 3, 321, "the reduction of critical constants," is, however, open to more serious objection.

**2. Vapour Densities.**—The classical methods of Dumas (1826), Hofmann (1868), and Victor Meyer (1878) are so well known and widely described as to require no discussion. The Victor Meyer method has the advantage that the temperature of the heated zone in which the substance is volatilised need not be known and, possibly for this reason, it has been developed and modified to a greater extent than the others. More compact modifications have been described by Weiser (*J. Physical Chem.* 1916, 20, 532) and by Macinnes and Kreiling (*J. Amer. Chem. Soc.* 1917, 39, 2350), and methods

depending on measurement of increase of pressure at constant volume by Bleier and Kohn (Monatsh. 1899, 20, 505) and by Lumsden (*J.C.S.* 1903, 83, 342). Very high-temperature determinations on substances of low volatility were carried out by Nernst (*Z. Elektrochem.* 1905, 9, 622; Wartenberg, *Z. anorg. Chem.* 1908, 56, 320) by use of iridium apparatus. For very reactive substances, or for determinations at elevated temperatures at which dissociation may occur, it is often advantageous to use all-glass apparatus of constant volume, and for this purpose a variety of all-glass pressure gauges is available. These are usually used immediately, as null indicators, between the closed vessel and the manometer proper (for references and brief descriptions, see L. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions," London, 1939).

Satisfactory micro-methods of vapour density determination have been devised (J. B. Niederl and V. Niederl, "Organic Quantitative Micro-analysis," London, 1938, pp. 175-183), depending on the displacement of mercury under controlled conditions. Two types of apparatus are shown

volatilise the substance under investigation. Some mercury is expelled by expansion and is weighed; this serves as a "blank" for the subsequent determination. After cooling, the mercury is removed and a weighed sample of substance (5-10 mg.), contained in a suitable

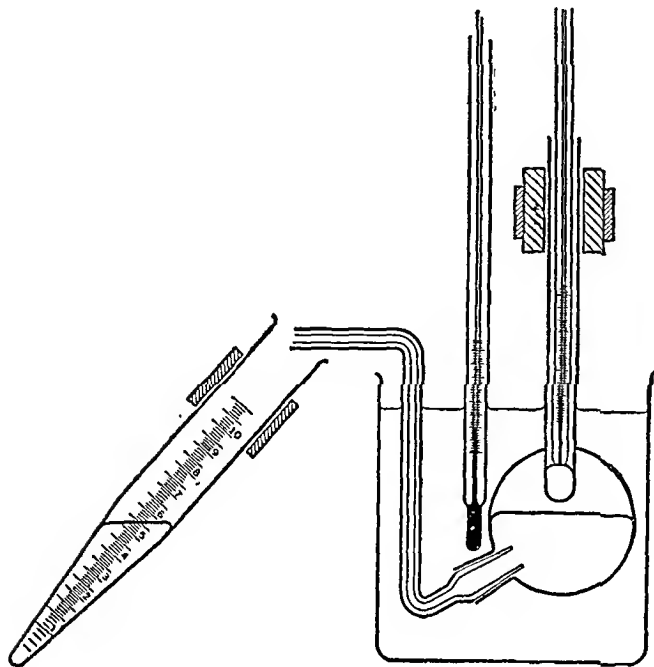


FIG. 3 (a).

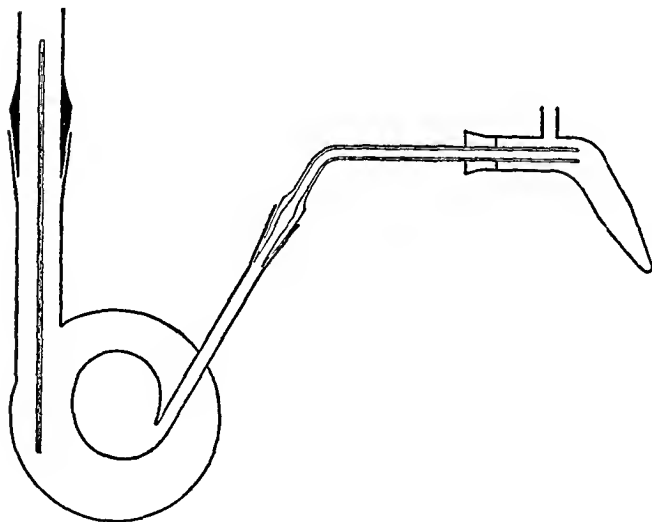


FIG. 3 (b).

in Figs. 3 (a) and 3 (b), the former for liquids boiling below 100°C. and the latter for less volatile substances. The vaporisation vessels and the associated capillary tubes are filled completely with pure, dry mercury at room temperature, and are heated in a liquid or vapour bath to a determined temperature sufficient to

volatilise the substance under investigation. Some mercury is expelled by expansion and is weighed; this serves as a "blank" for the subsequent determination. After cooling, the mercury is removed and a weighed sample of substance (5-10 mg.), contained in a suitable capillary tube or micro-pipette, is introduced into the vaporiser, which is again completely filled with mercury to the outlet of the capillary tube. The apparatus is then heated to the predetermined temperature and, when equilibrium is reached, the displaced mercury is weighed. The molecular weight of the substance is then given by the relationship  $M = wRT/PV$ , where  $w$  is the weight of the sample,  $R$  is the gas constant in ml.-mm. per degree,  $T$  is the temperature of the bath in °K., and  $P$  and  $V$  are the pressure and volume of the vapour, respectively.  $V = W - c\Delta T/d - v$ , where  $W$  is the weight of the displaced mercury,  $c$  is the correction for expansion per °C., previously determined,  $\Delta T$  is the difference between room temperature and that of the bath ( $T$ ),  $d$  is the density of mercury at  $T$ , and  $v$  is the volume of the liquid or solid sample introduced.  $P = p_1 + p_2 - p_3 + p_4$ , where  $p_1$  is the barometric pressure,  $p_2$  is the vertical distance between the mercury level in the vaporiser and the capillary outlet,  $p_3$  is the vapour pressure of mercury at temperature  $T$ , and  $p_4$  includes corrections for the temperature of the mercury in the vertical section of the capillary outlet, the conversion of the barometer to 0°C., and the capillary depression of mercury in the outlet tube. These corrections are to some extent self-cancelling, and can usually be omitted within the ordinary limit of accuracy of about 1%.

Methods of determining gas or vapour densities based on Graham's Law of diffusion, or effusion, do not seem to have found very wide use since they were applied by Bunsen ("Gasometrische Methoden," Braunschweig, 1875, p. 128), except in special cases such as

that of ozone (Soret, 1868; Ladenberg, 1898). It appears, however, that they are capable of providing convenient laboratory methods with an accuracy of the order of 1% for reasonably volatile substances (Eyring, J. Amer. Chem. Soc. 1928, 50, 2398).

The molecular weight of a substance of suffi-

cient volatility which is immiscible with water can be determined by steam distillation, a process which can be regarded as an indirect vapour-density method. The composition of the vapour from the distillation is solely a function of the respective vapour pressures of the immiscible components, i.e., the molecular ratio  $n_A/n_B$  in the distillate will be equal to  $P_A/P_B$ . Then a determination of the weight ratio  $W_A/W_B$  allows of calculation of the molecular weight of one component if that of the other is known, from the relationship

$$M_A = M_B(W_A P_B / W_B P_A).$$

The temperature of the distillation is accurately determined, and the value of  $P_B$ , i.e., the vapour pressure of water at this temperature, is found from recorded data;  $P_A$  is then barometric pressure less  $P_B$ .

## II. MOLECULAR WEIGHTS OF SUBSTANCES IN THE LIQUID STATE.

Since the molecular weights of substances are more conveniently determined under other conditions, this section is concerned simply with states of aggregation peculiar to the liquid phase; in very general terms, with the degree of association, or with the degree of ordered structure in the liquid. This subject is not strictly within the scope of the present article, but mention may be made of certain properties which are diagnostic of association, although they are not generally capable of giving any quantitative estimation of degree of association. Van der Waals's and Dieterici's equations of state predict that the critical ratio  $RT_c/P_c V_c$  should be constant for all substances and have the values respectively of 2.67 and 3.695. Most normal liquids give a value of about 3.7, but associated liquids give values which are considerably higher. Associated liquids also show abnormal surface tension relationships, although the methods proposed by Ramsay and Shields (J.C.S. 1893, 63, 1087) and others for the estimation of association by this means have been shown to be unreliable (S. Sugden, "The Parachor and Valency," London, 1930, pp. 157-180). Probably the best criterion is found in the entropy of vaporisation, which, for normal liquids, with very few exceptions, has a value of about 21 g.-cal. per degree at the boiling-point. This is expressed in Trouton's rule that  $Ml/T = \text{constant} = 21$ , where  $M$  is the molecular weight,  $l$  is the latent heat of evaporation per g., and  $T$  is the boiling-point in  $^{\circ}\text{K}$ . It is clear that associated liquids will show an abnormally high entropy of vaporisation, provided that the vapour produced is not itself associated; this can, of course, be investigated by vapour density measurements. Hildebrand (J. Amer. Chem. Soc. 1915, 37, 970) has proposed a more accurate form of Trouton's rule which shows the same effect.

## III. SOLUTION METHODS.

Methods based on the direct determination of osmotic pressures require such highly specialised technique that they are only used in special cases; they are suitable for dealing with substances of very high molecular weight (cf.

Carter and Record, J.C.S. 1939, 660), but this subject is discussed in another article. There are three other main methods based on colligative properties of solutions.

It should be realised that there is often a limitation in accuracy in these methods which is imposed by departure from the ideal laws, which cannot therefore be surmounted by elaboration of technique. It is, however, usually not of first importance that results should be accurate, so long as they give unequivocal evidence as to which, of a number of possible values of molecular weight, is the correct one. The precise value is then available from accurate analytical data. It is not within the scope of this article to discuss analytical methods; for example, determination of an equivalent by titration cannot be considered as a molecular weight determination.

It may be noted that some improvement of accuracy can be effected by comparing the "unknown" substance in solution with a standard substance in the same solvent at the same molar concentration; deviation from ideal behaviour will then mutually cancel to some extent. Abnormalities due to association or dissociation in solution cannot be discussed.

### 1. The Lowering of Vapour Pressure.

The vapour pressure of a solution is lowered below that of the pure solvent by the presence of a non-volatile solute. The relationship expressed in Raoult's Law,  $P/P_0 = N/(N+n)$ , where  $P$  and  $P_0$  are the vapour pressures of solution and solvent, respectively, and  $N$  and  $n$  are the respective molar quantities of solvent and solute in the solution, becomes, with sufficient accuracy in dilute solution,  $\Delta P/P = n/N$ , where  $\Delta P/P$  is called the "relative lowering of the vapour pressure." Hence, for  $w$  g. of solute, of molecular weight  $m$ , dissolved in  $W$  g. of solvent of molecular weight  $M$ ,  $m = wMP/W\Delta P$ . The methods available for the precise determination of vapour pressures can, of course, be applied to solutions, and the value of  $\Delta P$  obtained by comparison with the vapour pressure of the pure solvent determined in the same way. It is usually desirable, however, to determine  $\Delta P$  directly by a differential method, as in Menzies's method (J. Amer. Chem. Soc. 1910, 32, 1615), the apparatus for which is shown in Fig. 4. The side-arm of the apparatus is joined by a rubber connection, which can be closed with a clip, to a reflux condenser. Both inner and outer vessels initially contain pure solvent; with the clip closed, air is displaced from the apparatus by boiling the liquid in the outer vessel with the stopper removed; the liquid in the inner vessel is raised to the boiling-point by the stream of vapour passed into it by means of the inner re-entrant tube. When all the air

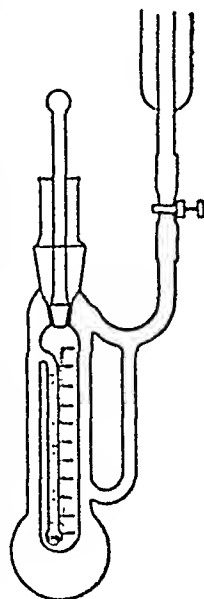


FIG. 4.

has been expelled, the stopper is inserted and the connection to the condenser is opened. The level of the liquid in the inner re-entrant tube, which is divided in mm. is observed. The whole procedure is repeated, with a weighed amount of solute added to the inner vessel, and in this case the observed level is depressed because of the excess vapour pressure of the solvent as compared with that of the solution. The difference between the two observations gives  $\Delta P$ , and  $P$  is equal to the barometric pressure. Knowledge of the density of the solution, or, within experimental error, of the solvent, at its boiling-point, is required. It is interesting to notice that the same apparatus can be used for vapour-density determinations (Menzies, *ibid.* 1910, 32, 1624).

An elegant micro-method depending on the identity of vapour pressures of equimolar solutions of different solutes in the same solvent (an "isopiestic" method) was devised by Barger (J.C.S. 1904, 85, 286) and has been developed by Rast (Ber. 1921, 54, 1979) and others. It has the great advantage that pure solvents are not required, and that the range of solvents available is not restricted by considerations of suitability of boiling- or freezing-points; valuable solvents such as pyridine, or even mixed solvents thus become available. In Rast's procedure (*l.c.*) a number of thin-walled capillary tubes,  $80 \times 1$  mm., are prepared, and the ends are drawn out hair-fine, a central section of the original diameter and 30–40 mm. long being left. Standard solutions of a suitable standard substance (preferably coloured, *e.g.*, azobenzene) are prepared, covering the concentration range of 0.1–1.0 molar, and a single solution, of known weight concentration, of the substance of which the molecular weight is required. The capillary tubes are held in a split rubber bung fitted to a filter tube, so that by applying gentle suction to the side-arm of the latter, the solutions can be drawn into the tubes. Each capillary is half filled with one of the standard solutions; a small air-bubble is then allowed to enter, and the filling is completed by drawing in the other solution in the same way. The air bubble now occupies a central position in the capillary. It must be arranged that a small air space is left adjacent to each drawn-out end, which can then be sealed off in the flame of a micro-burner. A set of capillaries filled in this manner, each containing a different standard solution, is suitably attached to a microscope slide so that the menisci of one or other of the solutions are all in line with a reference mark on the slide (etched, or formed by an attached hair). The alignment is carried out under a low-power microscope and the capillaries, preferably in a shallow water-bath to maintain constant temperature, are observed from time to time. In the case that the two solutions in a given capillary are of equal molar concentration, the position of the central bubble remains unchanged; in other cases, isothermal distillation of the solvent occurs across the bubble from the weaker solution to the stronger, so that the bubble is displaced in the direction of the weaker solution. The extent of the displacement is measured, and an interpolation can be made, if necessary, in order to find the molarity of the

standard solution which would be isopiestic with the solution of the substance under investigation. Finer discrimination can be obtained by means of a second experiment with suitably modified standard solutions. The time necessary for the observations varies very greatly according to the volatility of the solvent, and may have any value between 0.25 and 48 hours. The accuracy of the method is about 10%; possibly slightly better than this in the original method of Barger (*l.c.*). Other modifications, designed to avoid possibility of mixing of the two solutions (*e.g.*, Niederl and Levy, *Science*, 1940, 92, 225) are claimed to give greater accuracy.

Isopiestic methods on the large scale have been developed to a very high degree of precision, and have been used for accurate activity determinations (Sinclair, J. Physical Chem. 1933, 37, 495; Robinson and Sinclair, J. Amer. Chem. Soc. 1934, 56, 1830; Scatchard, Hamer, and Wood, *ibid.* 1938, 60, 3061).

2. **Ebullioscopic Methods.**—The classical methods and the principles involved are so well known and widely accessible as to need no special description. The chief difficulty is the avoidance of superheating, and a great number of forms of apparatus has been devised to overcome it. Probably the most satisfactory method is to heat the solution by passing into it a stream of vapour of the solvent (Sakurai, J.C.S. 1892, 61, 989; Landsberger, Ber. 1898, 31, 458; Walker and Lumsden, J.C.S. 1898, 73, 502; McCoy, Amer. Chem. J. 1900, 23, 353); but this is attended with the difficulty that the concentration of the solution is continuously, if gradually, changing during the course of the experiment. The best of other methods is that suggested by Cottrell (*ibid.* 1919, 41, 721; Read and Washburn, *ibid.* 1919, 41, 729), in which the thermometer bulb is continuously bathed in a stream of solution and bubbles of vapour, raised by a "vapour lift." Electrical heating is very advantageous, and an apparatus incorporating this, together with the Cottrell principle, is illustrated in Fig. 5; details for the construction of such an apparatus are given by W. G. Palmer, "Experimental Physical Chemistry," Cambridge, 1941, pp. 123–127. The necessity for a Beckmann or other sensitive thermometer is ingeniously eliminated in the apparatus devised by Menzies (Proc. Nat. Acad. Sci. 1921, 7, 81; Menzies, J. Amer. Chem. Soc. 1921, 43, 2309; Menzies and Wright, *ibid.*, p. 2314), shown in Fig. 6, in which a differential vapour-pressure thermometer is used. This instrument consists of a capillary U-tube, with one limb long and divided in mm., joining two small bulbs; this forms an enclosed system containing a suitable liquid sealed up with its vapour, air being absent. The lower bulb is bathed with vapour and solution by means of a Cottrell "vapour-lift," and is therefore at the boiling-point of the solution; the upper bulb, which is in the pure vapour, is at the boiling-point of the solvent. This difference in temperature is accurately registered by the level of the thermometric liquid in the divided vertical tube; knowledge of the densities and vapour pressures of this liquid at different temperatures is required. Water is usually suitable for the pur-

pose, and will cover a considerable range of solvents with different boiling-points. It will be noticed that this method eliminates errors due to variation of barometric pressure.

Still further improvements in technique have been introduced by Swientoslawski in his simple and differential ebulliometers (*Z. physikal. Chem.* 1932, A, 160, 257; *Bull. Soc. chim.* 1931, [iv], 49, 1563; W. Swientoslawski, "Ebulliometry," *Krakow*, 1936), which make use of the "vapour lift" principle.

Micro-methods for ebullioscopic molecular-weight determinations, based on Beckmann's and Cottrell's methods, have been described, and these are discussed in the article on MICRO-CHEMISTRY (v. this Vol., p. 74d). Information

relative rates of loss of heat of the system to the cooling bath and gain of heat due to the solidification of the solvent. In order to make the difference between this false equilibrium temperature and the true freezing-point as small as possible, it is necessary to ensure that the cooling bath is not at a temperature very much lower than the freezing-point. It will be noticed that the cryoscopic method, as compared with the ebullioscopic method, suffers from the disadvantage that the pure solvent phase with which the solution must come into equilibrium is a condensed phase (solid as compared with vapour), and this uses up, necessarily, a larger amount of material, with the attendant danger of disturbance of concentration. Further, the comparatively small latent heat of freezing makes the temperature measurements more susceptible to disturbance, although this is offset by a corresponding gain in the magnitude of the molecular depression constant (see this Vol., p. 164a). Many solvents with desirable properties for cryoscopic molecular-weight determinations are appreciably hygroscopic, a tendency which is aggravated at lower temperatures. In such cases a modification of the apparatus is necessary in order to protect the solution from atmospheric moisture; entirely enclosed apparatus with electromagnetic stirring is sometimes used for this purpose.

A very valuable modification of the cryoscopic method is made available by solvents of high molecular-weight, high freezing-point, and low latent-heat. Substances of this type have such high molecular depression constants that the significant temperature differences are large enough to be measurable with adequate accuracy by means of a thermometer divided in 0.2°C. in an ordinary melting-point apparatus (*Rast, Ber.* 1922, 55 [B], 1051, 3727). Camphor is the most commonly used solvent, requiring a thermometric range of 100–180°C., although other substances of the terpene series, with even higher depression constants, have been proposed (*Pirsch, ibid.* 1932, 65 [B], 862, 1227, 1839; 1933, 66 [B], 349, 506, 815, 1691; 1934, 67 [B], 101, 1115, 1303; 1935, 68 [B], 67). The camphor used must be of the highest purity, and the depression constant for each batch must be separately determined with a known standard solute, because of the very wide variations which are found, according to the source, natural or synthetic, of the camphor.

The method lends itself admirably to micro-technique, in which case only milligram samples of solute are required. A thin-walled glass capillary is prepared, 40 mm. long and 2 and 4 mm. wide, respectively, at the closed and open ends. A quantity of solute is introduced, with precautions to avoid scattering of the substance on the walls of the tube. The weight of the solute is determined by difference. A quantity of camphor, 10–20 times the weight of the solute, is similarly introduced, and the tube is sealed, introduction of moisture from the flame being avoided: the sealed end is pulled out into a small glass rod, about 5 cm. in length. A similar tube containing the pure camphor only is prepared at the same time. The tubes are attached to a thermometer bulb, and heated in

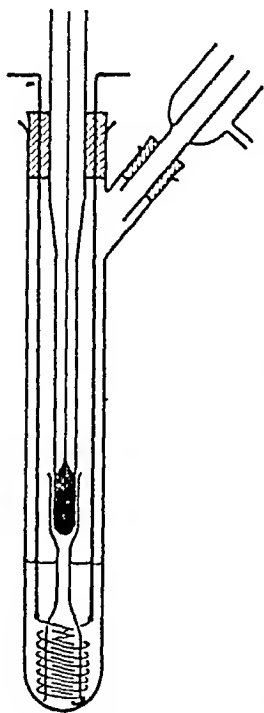


FIG. 5.



FIG. 6.

on molecular elevation constants for various solvents is given under MOLECULAR DEPRESSION AND ELEVATION CONSTANTS, this Vol., p. 164a.

3. Cryoscopic Methods.—The ordinary laboratory method is still essentially the same as that due to Beckmann (*Z. physikal. Chem.* 1888, 2, 638, and later papers) and involves a supercooling procedure. A number of experimental difficulties are encountered. If undue supercooling takes place before freezing commences, a considerable amount of solvent separates from the solution in the solid state, causing a very appreciable increase in the concentration of the residual solution as compared with that of the original, on which the calculations are usually based. This source of error is minimised by stirring and by inoculation with a small crystal of the pure frozen solvent. The steady temperature recorded by the thermometer when freezing has occurred may not be the true freezing-point of the solution; it is a resultant temperature which depends on the



a suitably stirred bath until a clear liquid melt is obtained, cooled until solidification occurs, reheated, and cooled again, in order to ensure homogeneity. The freezing-point is then determined with a rate of heating not exceeding 0.5° per minute, and is the temperature at which the last trace of crystalline camphor disappears. It must be emphasised that this is not the "melting-point" as ordinarily determined, which will, of course, be at a lower temperature (*i.e.*, it will be on the solidus curve and not the liquidus). If larger quantities of material must be used, in the absence of a micro-balance, a clear homogeneous melt must first be made in a sealed tube. After cooling, this is opened and the contents are powdered and introduced into a melting-point tube, which is then scaled.

Mention must be made of equilibrium methods of determining freezing-point depressions, as distinct from the super-cooling methods already described. In these, the solution is allowed to come into equilibrium with a large amount of pure frozen solvent under conditions of efficient heat-insulation. When equilibrium is reached, samples of the solution are withdrawn, and the concentration found by analytical methods. By such procedure, involving a direct comparison with a similar system consisting of pure solvent only, very precise determinations can be made, particularly when thermocouples, or resistance thermometers, are used to determine the temperature difference. Usually large amounts of material are required, and the apparatus is so specialised as to be inaccessible for ordinary laboratory procedure (Adams, *J. Amer. Chem. Soc.* 1915, 37, 481; Havorka and Rodebush, *ibid.* 1925, 47, 1614; Randall and Scott, *ibid.* 1927, 49, 647; Scatchard and Prentiss, *ibid.* 1932, 54, 2676).

#### IV. MOLECULAR WEIGHTS OF SUBSTANCES IN THE SOLID STATE.

The only method available is that of X-ray diffraction, and the apparatus and technique is so highly specialised that a description is beyond the scope of the present article. Nevertheless, it possesses such unique advantages in certain cases that some mention must be given to it. It requires only a single crystal of the substance to be examined, and this may be of considerably less than a milligram in weight, and remains quite unaffected by the process of the determination. The principle of the method depends on finding the dimensions of the unit cell of the crystal and the number of structural units which it contains. A determination of the density of the substance, which can be done by a flotation method in a medium in which it is insoluble, allows of an accurate assessment of molecular weight. It is clear that this method may be of great value in the case of precious substances available only in the minutest quantity, and required for further investigation (W. H. and W. L. Bragg, "The Crystalline State," London, 1933, pp. 238-240).

**D. J. G. I.**  
**MOLYBDENITE.** A mineral consisting of molybdenum sulphide,  $\text{MoS}_2$ , crystallising in the hexagonal system in the form of six-sided plates or short, slightly tapering or barrel-

shaped prisms; usually occurs in disseminated scales, and sometimes in foliated or granular masses. Possesses a perfect basal cleavage, the laminae being very flexible, but not elastic. The mineral is sectile, can be easily scratched by the finger-nail, and has a greasy feel. Its colour is lead-grey with a faint bluish tinge, the streak on paper being bluish-grey and on porcelain a greenish-grey, whilst the lustre is metallic.  $\rho$  4.7. Molybdenite is often confused with graphite, but the latter has less than half the density of molybdenite, besides having a black, shining streak.

Molybdenite is the only important source of molybdenum. It occurs as disseminations and segregations in granite, as "pockety" deposits in pegmatites, in limestones adjacent to granite, and in quartz veins. The annual world production of molybdenum since 1940 has exceeded 16,000 tons, of which the United States has contributed more than 90%, mainly from the famous molybdenite mine at Climax, Colorado. During most of the nineteen-thirties this single mine produced from 80 to 85% of the world's molybdenum, but within recent years this percentage has dropped to about 60, owing to the greatly increased recovery of by-product molybdenum from the copper ores of Utah and New Mexico, which contain minute amounts of molybdenite. Molybdenum is principally used as an alloying element in the manufacture of special grades of iron and steel, notably in high-speed tools, rustless steels, dies, and permanent magnets. It serves best in steels in combination with nickel and chromium, and is reckoned to have twice the hardening power of tungsten. High molybdenum steels, with more than 1% Mo, are made from ferromolybdenum, but low "molly" steels, as they are referred to in the trade, are made by adding calcium molybdate (*see also* this Vol., p. 220d). Minor quantities of molybdenum are used for catalysts, dyes, pigments, and inks, and in the form of ammonium molybdate it serves as a chemical reagent, as a fire-proofing material, and as a disinfectant.

*References.*—R. H. Rastall, "Molybdenum Ores," Monogr. Imperial Institute, London, 1922; V. L. Eardley-Wilmot, "Molybdenum, Metallurgy and Uses, and the Occurrence, Mining and Concentration of its Ores," Mines Branch, Canada, 1925, No. 592; F. L. Hess, "Molybdenum Deposits," U.S. Geol. Survey, Bull. 761, 1924; B. S. Butler and J. W. Vanderwilt, "The Climax Molybdenum Deposit of Colorado," U.S. Geol. Survey Bull. 846-C, 1933. In the *British Isles*: Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 1916, Vol. V, 2nd ed., 1917.

**D. W.**  
**MOLYBDENUM.** Sym. Mo. At. wt. 95.95. At. no. 42. Molybdenum consists of seven isotopes of which the masses and percentage abundances are  $^{92}\text{Mo}$  15.5,  $^{94}\text{Mo}$  8.7,  $^{95}\text{Mo}$  16.3,  $^{96}\text{Mo}$  16.8,  $^{97}\text{Mo}$  8.7,  $^{98}\text{Mo}$  25.4, and  $^{100}\text{Mo}$  8.6% (Mattauch and Lichtblau, *Z. physikal. Chem.* 1939, B, 42, 288), which give an atomic weight of 96.03.

#### HISTORY.

Molybdenite, the sulphide ore, was known to the ancient Greeks and others, who confused it with lead because of its heaviness, and with



graphite because in appearance it is similar to this mineral. Up to the eighteenth century graphite and molybdenite were sold as "molybdän" or even "molybdænum," a name derived from "molybdis" or "molybdæna" (from the Greek *μολύβδινα*, lead), terms used to designate minerals which appeared lead-like. Scheele in 1778 showed that molybdenite and graphite were entirely different, for with nitric acid molybdenite was converted into a white solid which he called "molybdenic acid." When his colleague Bergman suggested that this body was probably an oxide of a new metal, Scheele, having no suitable furnace, asked P. J. Hjelm of Stockholm to reduce it to the metal. Hjelm ground the white molybdic acid to a paste with linseed oil, and heated it in a closed crucible to carbonise the oil and to reduce the oxide; he thus obtained the new element in metallic form in 1782. It was not, however, until about 1890 that the metal was carefully investigated in view of its possible value as an alloy addition to steel. The approximate world production of the metal has shown a great increase in recent years, as indicated by the following figures: 1900 10 tons; 1930, 2,000 tons; 1941, 17,000 tons; of the last figure over 15,000 tons were produced in the U.S.A.

#### OCCURRENCE.

(See also MOLYBDENUM MINERALS, this Vol., p. 226a.)

Molybdenum does not occur in the metallic state, and although its compounds are fairly widely distributed in small quantities, comparatively few definite molybdenum minerals are recognised. The most important ore is *molybdenite*,  $\text{MoS}_2$  (v. this Vol., p. 216b). A colloidal form of molybdenite has been described and named *jordisite*. Other common minerals are *wulfenite*,  $\text{PbMoO}_4$ , found in the oxidised portions of lead deposits in many parts of the world, *powellite*,  $\text{CaMoO}_4$ , and *molybdite* or *molybdic ochre*,  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7.5\text{H}_2\text{O}$  (v. this Vol., p. 226b), the yellow oxidation product of molybdenite. Less common minerals are *chillagite*,  $3\text{PbWO}_4 \cdot \text{PbMoO}_4$ , *illsemaninite* or blue oxide,  $\text{MoO}_2 \cdot 4\text{MoO}_3$ , *koechlinite*,  $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$ , and *lindgrenite*,  $2\text{CuMoO}_4 \cdot \text{Cu}(\text{OH})_2$ . A magnesium molybdate, *belonesite*,  $\text{MgMoO}_4$ , and a cobalt molybdate, *pateraite*,  $\text{CoMoO}_4$ , have also been described. Molybdenum occurs in small quantities in other minerals containing the rare heavy metals of the same group (tungsten, vanadium, etc.).

Small quantities of molybdenum are found in various igneous and sedimentary rocks, as well as in ground waters, hot spring waters, and plant and animal tissues. In the case of igneous rocks, molybdenum is more frequently present in siliceous rocks such as granites, but small quantities have been found also in basic and ultra-basic rocks. Molybdenum has also been found in sedimentary rocks, especially shales and, generally accompanied by vanadium, in clays; it has been reported to be present in the manganese nodules collected by the Challenger expedition. Molybdenum has been found in spectroscopic amounts in spring waters in Brazil,

Spain, and Japan, and also in sea water. The most important occurrence in thermal waters is that reported by Zeis (Nat. Georg. Soc., Katmai Ser. 1929, Vol. 1, no. 4) in the Valley of Ten Thousand Smokes, Alaska, where molybdenum is deposited as "molybdenum blue" around a steam vent. From his work on the study of coal ash, Goldschmidt (Ind. Eng. Chem. 1935, 27, 1100) concludes that the content of molybdenum in this material is higher than in average rocks, and the ash from oil-burning steamers was found by Herman (Metallwirts. 1936, 15, 1124) to contain Mo 0.1, Ni 0.5, and V 2.5%.

The presence of molybdenum has been reported in milk and also in hen eggs. In plant products molybdenum is frequently reported, Rao (Sci. and Cult. 1938, 4, 362) found 8-11 p.p.m. in peas. Dingwell, McKibbin, and Beans (Canad. J. Res. 1934, 11, 32) found the metal in numerous plants, but not always in the soil in which the plants grew, and no molybdenum was found in similar plants from other areas. According to Menlen and Ravenswaay (Proc. Acad. Sci. Amsterdam, 1935, 38, 7), leaves of Virginia creeper, poplar, and lilac contain small amounts of molybdenum.

Although molybdenum has been found on every continent and in many countries, only three deposits of molybdenite are important producers of the metal. These occur at Climax, Colorado; Questa, New Mexico and Knaben, Norway. Smaller quantities are found in Peru, Canada, Australia, Chile, U.S.S.R., etc.

Certain copper ore-bodies produce molybdenite as a by-product in Canada, Sonora, Mexico; Braden, Chile; Copper Creek, Arizona, etc. Wulfenite is found in the oxidised parts of lead deposits in many places, especially Arizona, New Mexico, South America, Northern Africa, Spain, and U.S.S.R., and is believed to be formed by molybdenum-bearing thermal waters coming in contact with oxidised lead deposits. Powellite is only a minor source of molybdenum as a by-product in the recovery of scheelite for tungsten; this mineral, together with molybdite, constitutes the usual oxidation product of molybdenite.

The average molybdenite content of commercial ore-bodies as mined is approximately 1%, which is disseminated throughout the rock in small grains; after fine grinding, concentration of the molybdenite by froth flotation is a relatively simple metallurgical operation. Its separation from copper has been successfully carried out in the U.S.A., Mexico, and South America. The usual grade of concentrate obtained contains  $\text{MoS}_2$  75-85%, objectionable impurities being arsenic, bismuth, antimony, phosphorus, and copper. Wulfenite is easily wotted and is usually separated from its accompanying gangue by water concentration.

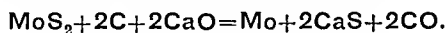
#### REDUCTION OF MOLYBDENUM CONCENTRATES.

By far the largest proportion of molybdenum produced is used in the iron and steel industries, and one method of introducing the metal is in the form of ferromolybdenum.

Ferromolybdenum was formerly produced from molybdenite concentrates by roasting to oxide and reducing with carbon in the presence

of scrap iron, in crucibles, but in most cases it is now made in electric furnaces by fusing the concentrates, either in the raw state or after a preliminary roast with varying proportions of coke, lime, scrap iron, etc.

In one plant, the raw concentrates containing  $\text{MoS}_2$  40–90% and averaging 75% were treated direct in a single-phase electric furnace, which was water-jacketed and lined with silica and fire-brick. The lower electrode was of bronze or copper and the upper of graphite, and a current of 3,500–4,500 amp. at 50 v. was used. For every 100 parts of concentrates containing  $\text{MoS}_2$  75 and Fe 9%, 120 parts of lime, 10 of coke, and 5 of scrap iron or steel turnings were added; the furnace was tapped every 4 hours, and the ferromolybdenum produced contained Mo 70, S 0.4, and C 4.0%. The sulphur in the molybdenite was almost entirely taken up by the slag or converted into sulphur dioxide;

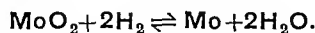


In another plant, the molybdenite concentrates were first converted into oxide by roasting. The resulting oxide was leached with a strong solution of ammonia and filtered. The solution was then strongly heated until the ammonia was driven off, crude molybdic oxide being left; this was reduced in an electric furnace with coke and steel scrap turnings, the current used being 4,000–5,000 amp. at 55 v. The costs of this process were considered high owing to mechanical loss during the preliminary treatment of the concentrates, and direct reduction without roasting was resorted to, lime, coke, and steel turnings being used as additions to the charge. This proved the more satisfactory process and over 80% of the molybdenum fed in as concentrates was recovered in the ferromolybdenum, the chief losses being 11% by dusting and 7% in the slag. The dusting loss was recovered by the use of filter bags, and some 90% of the slag loss was recovered by table concentration.

The ore wulfenite or lead molybdate has also been used as a source of ferromolybdenum. In this case, as described by Keeney (Trans. Amer. Inst. Min. Met. Eng. 1920, 62, 28), the ore is first treated with soda ash in a lead furnace, lead bullion and a sodium molybdate slag being produced. The slag is crushed, mixed with lime, iron ore, and carbon, and smelted in an electric furnace lined with magnesia.

**Reduction by Hydrogen.**—Pure molybdenum, especially when required for the production of sheets, wire, etc., is generally obtained by hydrogen reduction. Molybdenite is first roasted to oxide in a suitable furnace, the oxide is dissolved in ammonia, the solution is filtered, and nitric acid is added. This precipitates relatively pure molybdic acid, which is ignited at a temperature below  $1,000^\circ$  to molybdic oxide. The ignited oxide is placed in trays and treated in the tubes of a suitable furnace, a stream of purified and dried hydrogen being passed through the heated tubes. The reduction is commenced at a low temperature ( $300^\circ$ ), for at this temperature the more volatile molybdenum trioxide,  $\text{MoO}_3$ , is reduced to the less volatile dioxide,  $\text{MoO}_2$ . The reduction of

the dioxide to metal begins at  $500^\circ$  and is fairly rapid at  $600^\circ$ .



The reverse reaction occurs to a negligible extent below  $700^\circ$ . At  $800^\circ$  equimolecular proportions of hydrogen and water vapour have no effect, but proportions of water above this ratio result in the formation of molybdenum dioxide; proportions below this ratio give metal. The reduction of molybdenum is more difficult than the corresponding reduction of tungsten, it being frequently necessary to run the furnace for 40 hours.

The metal powder thus obtained is removed from the boats, screened, and pressed into bars in a hydraulic press, the process varying from that for tungsten in minor details only. The pressed bars are placed between the electrodes of an electric furnace and heated to about  $2,400^\circ$  by passing a suitable electric current through them, this operation being carried out in an atmosphere of hydrogen. The metal shrinks considerably during this process, and a suitable follow-up of the electrodes must be arranged for. The metal so obtained is rolled into sheets or swaged into round bars which are subsequently drawn into wire.

A hydrogen reduction method has also been used for the preparation of molybdenum-tungsten alloys, for which a mixture of the oxides of the two metals is reduced in hydrogen; the mixture may or may not be compressed into sticks before reduction.

**Other Methods of Reduction** include the following:

1. Reduction of the oxide (either the trioxide or preferably the less volatile dioxide) by means of carbon in crucibles.
2. Reduction of the oxide by the aluminothermic process, in which a mixture of 100 parts of the oxide and 38 parts of finely divided metallic aluminium is ignited by means of a piece of magnesium ribbon surrounded by barium peroxide on the surface of the charge. The mixture is contained in a suitable crucible, together with fluxes such as calcium fluoride, 50 parts being useful in moderating the reaction.
3. Reduction of the oxide by silicon, or by means of ferrosilicon if ferromolybdenum is required as the product. In this case also, lime may be added to assist the slagging off of sulphur.

The products of electric furnace reduction or reduction by means of carbon are liable to be high in carbon owing to the formation of carbides. These products may be decarburised by remelting with molybdenum oxide or by means of iron oxide and lime.

#### MISCELLANEOUS METHODS OF EXTRACTION.

Many processes have been worked out and patents obtained for the extraction of molybdenum from its ores; among these the following may be mentioned:

1. The Becket and Holladay Process consists in leaching the ores with a solution of

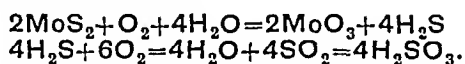
an alkaline sodium compound for a complete extraction of the metal, a substantial proportion of the impurities in the ore being left in the residue. The molybdenum is recovered by precipitation as calcium molybdate, which is then smelted or otherwise utilised.

2. The Doerner Process consists in briquetting the molybdenum concentrates with sodium chloride, mixed with a sulphur-bearing material if insufficient sulphur is present, and heating in a vertical retort to volatilise chlorides or oxychlorides of molybdenum.

3. Another Doerner Process comprises treatment of molybdenum ore at about 500° in a stream of chlorine gas. The molybdenum is volatilised as chlorido or oxychloride, which may be condensed and collected, or decomposed by steam or water into the oxide and hydrochloric acid. By maintaining the condenser at 200° the hydrochloric acid may be separated from the oxide and recovered in a separate condenser.

4. The Forland Process is similar to the above and consists in bringing the dried concentrate into contact with chlorine gas at a temperature above 268°. Molybdenum chlorido distils over and is separated from the sulphur, and from any metal chloride having a lower boiling-point, by fractional condensation. In case the material treated contains metals of which the chlorides have a higher boiling-point than that of molybdenum chloride, the temperature may be so controlled that these chlorides remain in the residue, from which they are recovered by leaching.

5. The Robertson Process consists of the direct volatilisation-roasting of the molybdenite concentrate in a highly oxidising atmosphere at about 800°. The process is hastened by the addition of steam, according to the following equations:



After cooling, the molybdenum oxide is drawn from a dust-collecting tower into a bag-house, where it is collected. For woollen bags the temperature must not exceed 120° and for cotton bags 90°.

6. For the treatment of wulfenite, in addition to the smelting method already described, an alkaline leach method has been used by Bonardi (Chem. Met. Eng. 1919, 21, 364). The material is treated with a boiling solution of sodium sulphide, which dissolves the molybdenum, the lead, together with any precious metals, being left as a residue suitable for smelting. The molybdenum goes into solution as sodium molybdate, and is finally precipitated, by addition of calcium chloride, as calcium molybdate, which may be reduced to ferromolybdenum or used directly in the manufacture of special alloy steels.

#### PROPERTIES.

Molybdenum is a silvery-white metal, malleable and ductile, and too soft to scratch glass, its Brinell number being 147. It can be filed and polished with ease. Its appearance and properties depend to a large extent on its

method of production. When obtained by the reduction of the oxide or sulphide by hydrogen it is a grey powder which may be compacted, by sintering and swaging at a high temperature, into a silver-white solid, but brittle, bar. When produced by the aluminothermic processes, it is compact, but usually contains iron and silicon as impurities; when obtained by reduction in the electric furnace it is also compact but, owing to the absorption of carbon, it has different properties from those of the carbon-free metal. Ductile forms of molybdenum, obtained by the compression and working of the pure metal prepared by hydrogen reduction, can be drawn into fine wire or rolled into ribbons and sheets. Molybdenum has a body-centred cubic structure, 2 atoms per unit cell,  $a=3.143 \text{ \AA}$ , which gives a calculated density of 10.2. The coefficient of expansion is approximately  $5.1 \times 10^{-6}$  between 0 and 500°. Its melting-point is about 2,550°, and its boiling-point about 3,600°. The density was reported by Moissan to be 9.01, but more recent determinations show that it increases with the amount of mechanical work put upon the metal up to about 10.3. The tensile strength of the pure metal increases with the fineness of the wire tested and varies from 200,000 to 300,000 lb. per sq. in., which is about half that of similar wires of tungsten. The electrical resistance is 5.6 microhms per cm. cube for hard-drawn wire and 4.8 for annealed wire. The temperature coefficient of electrical resistance between 0° and 170°C. is 0.005 and the specific heat is 0.0722 g.-cal. per g. per °C.

Crude molybdenum, the electric furnace product made direct from molybdenite, has a composition of approximately Mo 92, Fe 2, C 6%; it is very brittle and has a hardness greater than that of quartz. It melts at a lower temperature than pure molybdenum, and its specific gravity varies from about 8.6 to 8.9, according to the amount of carbon present. When pure molybdenum is embedded in carbon and heated to 1,500°, it absorbs carbon and becomes hard and brittle; if this carburised metal is melted with molybdenum dioxide, the carbon present is oxidised, and the metal is refined and its properties approach those of the pure metal. Molybdenum burns in oxygen at 500–600° with great brilliancy, even after the source of heat is removed. The metal is very slowly oxidised at ordinary temperatures and retains its lustre almost indefinitely, especially when in the form of drawn wire. It is slowly oxidised by steam. On prolonged heating at a dull red heat in air, it becomes covered with a white coating of molybdenum trioxide, and at 600° it oxidises rapidly and the trioxide thus formed sublimes. The pure metal is not volatile except at exceedingly high temperatures.

Molybdenum is attacked by fluorine at ordinary temperatures and by chlorine at a dull red heat, but it is not appreciably affected by iodine at temperatures as high as 700–800°. The metal is attacked by nitric acid and by hot concentrated sulphuric acid, but is not affected by hydrochloric acid. Fused oxidising salts such as potassium chlorate, nitrate, etc., attack it rapidly, but fused alkalis act only slowly on the metal.

## USES.

Molybdenum, in the form of wire, is used for supporting the filaments in incandescent electric lamps. It is also used for the winding of electric resistance furnaces, and for this purpose it has proved both cheaper than and superior to platinum, because of the quicker heating and higher temperatures attainable; for this purpose, however, the metal must be protected from the air to prevent oxidation. Molybdenum has been successfully substituted for platinum and for platinum-iridium alloy in electrical and other applications of these materials, such as in electric contact-making and -breaking devices. The Coolidge X-ray tube and a voltage rectifier have a considerable proportion of ductile molybdenum in their construction. For jewellery purposes it is a good substitute for platinum, being permanent in lustre, free from tarnish, capable of being worked like platinum, and very much cheaper. The metal has also been used for arc-lamp electrodes, by means of which a brilliant arc can be obtained. Molybdenum wire, in conjunction with tungsten wire, can be used in thermocouples for the measurement of high temperatures. The advantage of this type of couple is the higher melting-point of the elements as compared with the more usual platinum/platinum-iridium or platinum/platinum-rhodium couples; the disadvantage is that the elements oxidise at high temperatures, but protection may be supplied by a covering of fused magnesia or some similar material. A considerable amount of molybdenum is used in the anodes of radio valves and in other electronic devices; the low coefficient of expansion of the metal allows it to be sealed to Pyrex glass. In dentistry, gold-covered molybdenum wire has been used to a considerable extent. The main use of molybdenum is as an alloying element, particularly in the steel industry, only a little being used in non-ferrous alloys (*see below*). Molybdenum compounds are used to a limited extent in the chemical and ceramic industries, as for example for giving a yellow colour to pottery glazes and a red or yellow colour to glass. They are used as pigment colours in paints, lacquers, and printing inks, and in dyes for furs, hair, skins, etc.

## ALLOYS.

By far the largest proportion of molybdenum produced is used as an alloying-element addition to steels, and particularly to special alloy steels, and it is used, not like manganese as a scavenger, desulphuriser, and deoxidiser, but as a definite alloying element, its function being to enhance certain useful properties of the resulting metal, to add new properties, or to remove certain inherent weaknesses. Unlike manganese also, it is not lost by oxidation on remelting or reworking-up of scrap metal containing the element. It is found to be a useful addition to plain carbon steels and also to various classes of alloy steels, to which molybdenum imparts a uniformity of physical properties from the outside to the centre of sections, an absence of temper-brittleness, as shown by impact tests after slow cooling from the tempering tempera-

ture, and a close relationship between the limits of proportionality and the yield point. It causes a refinement of grain, increases the tensile strength, improves wear-resistance and resistance to fatigue, and promotes depth-hardening. To plain carbon steels 0.4-1.0% of molybdenum is added when these are to be used at high temperatures, as in turbine covers, rotors, steam cylinders, valves, etc., which operate at temperatures up to 400-500°. 0.5% of molybdenum and above has been found to double the strength of such steels at high temperatures, and to reduce effectively the rate of creep under the same conditions. Molybdenum to the extent of 0.3% is added to nickel structural steels containing Ni 1-3%, and is found to increase the yield point, elastic limit, and impact value of these steels without any sacrifice of elongation or reduction of area. The same quantity is also added to nickel case-hardening steels, as it promotes strength and toughness of core. Molybdenum, 0.25-1.0%, is also a useful addition to chrome-nickel steels which are liable to be highly stressed; it ensures absence of temper-brittleness as well as increasing the mechanical properties and reducing the effects of mass; these steels are used for coupling, connecting, and piston rods, high-pressure steel cylinders for the storage and transportation of gases, etc. Molybdenum is also a useful constituent of: (a) high-speed steels and cutting alloys, in which it can replace twice its weight of tungsten; (b) permanent-magnet alloys of the cobalt-tungsten type; (c) heat-resisting steels, which may also contain chromium, nickel, tungsten, etc. (used for aero-engine valves, etc.); (d) various corrosion-resisting steels; and (e) nitrogen-hardening steels, both of the chrome-aluminium and of the chrome-nickel variety, which are required to possess an intensely hard surface.

Molybdenum additions may be made to steel produced in open-hearth furnaces, in converters, in rotary pulverised-fuel furnaces, in electric furnaces, or in crucibles, and the molybdenum may be added in various forms. When added to molten steel as ferromolybdenum, it will readily dissolve in the metal in spite of its high melting-point, although molybdenum is oxidised by air at the temperature of molten steel. Molybdenum trioxide, when brought into contact with molten steel, is reduced to metal, but this oxide volatilises at the high temperature involved, and when it is used as an addition agent, some compound (such as calcium molybdate) must be used, or a protecting agent introduced.

Ferromolybdenum containing Mo 70-80, C 0.1, S 0.02% may be added during any of the steel-making processes, but is frequently replaced by cheaper materials, such as the following: (a) calcium molybdate containing Mo 40-50, CaO 20-25,  $\text{Fe}_2\text{O}_3$  4,  $\text{SiO}_2$  5-10, and S 0.04%; (b) molybdenum trioxide briquettes, Mo 49-52,  $\text{Fe}_2\text{O}_3$  4.0, S 0.25%; (c) a mixture of molybdenum trioxide and a sulphur-free pitch binder, briquetted under hydraulic pressure ("*Molyte*"), supplied by High Speed Steel Alloys of Widnes, containing Mo 40-50,  $\text{Fe}_2\text{O}_3$  5.0,  $\text{Al}_2\text{O}_3$  3.0, CaO 7.0

S 0.05%. All these products are packed in suitable containers.

Molybdenum sulphide,  $\text{MoS}_2$ , in the form of molybdenite concentrates containing Mo 48-55, Fe 3.0, S 34-37%, is sometimes added as such to steels for the purpose of improving the machinability, especially of chromo and nickel-chrome stainless steels, 0.5% of molybdenum and 0.5% of sulphur being required for this purpose.

Among non-ferrous alloys are the molybdenum-cobalt-chromium alloys known as "*Stellite*" (v. Vol. III, 217b, c). Haynes, the inventor of "*Stellite*," states (Trans. Amer. Inst. Min. Eng. 1913, 44, 576) that when molybdenum is added to a cobalt-chromium alloy so that the chromium is maintained at 15%, it rapidly hardens as the molybdenum content increases up to 40%, when the alloy becomes exceedingly hard and brittle. It cuts keenly and deeply into glass, and scratches quartz crystals with ease. It takes a beautiful polish, which it retains under all conditions, and on account of its extreme hardness, its surface is not readily scratched. When 25% of molybdenum is added to a 15% chromium-cobalt alloy, a fine-grained metal results which scratches glass somewhat readily, and takes a strong keen edge. Its colour and lustre are magnificent, and it will doubtless find a wide application for fine, hard cutlery. A typical analysis is Mo 22, Co 60, Cr 11, Fe 3, Mn 2, and C 1%.

#### C. O. B.

Molybdenum-tungsten alloys show a continuous series of solid solutions, and in the form of wire have been used in conjunction with tungsten wires in thermocouples for the determination of very high temperatures.

Molybdenum-nickel alloys containing up to 62% of molybdenum have been used as catalysts in ammonia synthesis.

### COMPOUNDS OF MOLYBDENUM.

Molybdenum compounds are usually classified according to valency, viz. the bi-, ter-, and quadri-valent compounds, which are basic, and the quinque- and sexa-valent series, which are acidic in character. Several of these series are, however, very scantily represented, and it is therefore simpler, if less logical, to treat molybdenum compounds according to their other constituents.

#### MOLYBDENUM OXIDES.

Molybdenum Sesquioxide,  $\text{Mo}_2\text{O}_3$ , may be present in the dark powders formed during the reduction of higher oxides by hydrogen, carbon monoxide, etc., but materials so reported are of doubtful individuality. A hydroxide or hydrated oxide is precipitated by ammonia from solutions of tervalent molybdenum salts (oxygen being rigidly excluded), and on drying at 100° this is reputed to leave  $\text{Mo}(\text{OH})_3$ , which is black and difficultly soluble in acids. This substance is also formed by cathodic reduction of molybdates in solution.

Molybdenum Dioxide,  $\text{MoO}_2$ .—This oxide is fairly well defined and is formed by gentle reduction of the trioxide in hydrogen (e.g., at 470°), excess  $\text{MoO}_3$  being removed by re-

placing the hydrogen by hydrogen chloride, which converts it into the volatile  $\text{MoO}_3 \cdot 2\text{HCl}$ . This oxide is also formed by heating ammonium molybdate alone, or sodium molybdate with zinc, out of contact with air. It forms opaque tetragonal crystals with a violet reflex, which have been found to possess a structure of the rutile type ( $a=4.86$ ,  $c=2.79$  Å.). These crystals are insoluble in boiling hydrochloric acid or potassium hydroxide solutions. By reducing molybdates in solution and then precipitating with alkalis, a number of dark greenish products have been reported which may contain hydroxides or hydrated oxides of quadrivalent molybdenum, but these derivatives are of doubtful individuality.

Molybdenum Pentoxide,  $\text{Mo}_2\text{O}_5$ .—Wardlaw and Nicholls (J.C.S. 1925, 127, 1488) prepared this oxide by heating the oxysulphate (produced by electrolytic reduction of the trioxide in sulphuric acid) in a stream of nitrogen; it formed a violet-black powder, insoluble in water, difficultly soluble in hydrochloric or sulphuric acid.

Molybdenum Trioxide,  $\text{MoO}_3$ .—This is the best known and principal oxide of molybdenum, and it occurs naturally in small quantities. It is usually prepared from the natural sulphide by powdering and roasting in the air. On a small scale the resultant oxide may be purified by sublimation, but on a larger scale it is usual to fix basic impurities by conducting the roasting in presence of silica and extracting the molybdenum trioxide with dilute ammonia; any copper passing into solution is precipitated with ammonium sulphide, and the ammonium molybdate recovered and recrystallised; the trioxide is obtainable from ammonium molybdate by evaporation with nitric acid or by ignition in a stream of oxygen. Impure molybdenum trioxide obtained by the action of acids on native molybdates is also dissolved in ammonia and purified in this manner. The trioxide is colourless, yellow when hot, and melts at 791°; the crystals deposited from the melt, often retaining a somewhat yellow tint, are rhombic ( $a:b:c=0.3872:1:0.4792$ ) with a density of 4.7, and are volatile above 500°. Gaseous hydrogen chloride at 150-200° converts the trioxide into  $\text{MoO}(\text{OH})_2\text{Cl}_2$ , which is readily volatile; chlorine produces  $\text{MoO}_2\text{Cl}_2$  with difficulty, and carbon monoxide, ethylene, and the like reduce it to coloured lower oxides. On boiling with aqueous hydrochloric acid a blue solution is formed, owing to partial reduction. Molybdenum trioxide has been proposed as an addition to pigments for paints and rubber, but it is photosensitive in presence of organic matter (becoming yellow and green) its applicability thus being limited (Gardner, Sci. Sect. Nat. Paint, Var. Assoc. Circ. 1936, No. 513).

Molybdic Acids.—Two fairly definite molybdic acids are known, viz. white  $\text{H}_2\text{MoO}_4$ , deposited in thin prisms by slow evaporation of a solution of the trioxide in nitric acid, and yellow  $\text{H}_4\text{MoO}_6$ , which slowly deposits from nitric acid solutions of ammonium molybdate. The former is characterised by a lower solubility, particularly in warm solutions (of the order of 0.5 parts per 100 of water at 80°, as against 1.7

parts for the yellow acid), but solution probably tends to cause a change of constitution, as the solubility is greater if the temperature at which measurements are made is approached from higher temperatures. Many other molybdic acids have been described, including some gummy materials, which are in many cases probably mixtures or colloidal dispersions. Molybdate ions tend to pass into polymolybdate ions in acid solutions in the same manner as do chromates, so that the nature of the predominating ion, and the acid or salt which may form a solid phase, are determined largely by the pH of the solution (Britton and German, J.C.S. 1930, 2154). Jander *et al.* (Z. anorg. Chem. 1930, 194, 383) used methods based on diffusion coefficients to show that at pH values greater than 6.5 the  $\text{MoO}_4^{4-}$  ion is stable; from pH 6.5 to 4.5 it is the  $\text{Mo}_3\text{O}_{11}^{3-}$  ion; from pH 4.5 to 2.9,  $\text{HMo}_6\text{O}_{21}^{3-}$ ; and from pH 2.9 to 1.5,  $\text{H}_3\text{Mo}_6\text{O}_{21}^{3-}$ . The crystalline acids and salts which have been described fall into a far larger range of classes than these, and must perhaps be regarded as acid, double, and hydrated salts derived from them.

**Molybdates.**—The following types of molybdate are known (M representing a univalent metal atom):  $\text{M}_2\text{O}, \text{MoO}_3$  (normal),  $2\text{M}_2\text{O}, \text{MoO}_3$  (di-),  $5\text{M}_2\text{O}, 12\text{MoO}_3$  or  $3\text{M}_2\text{O}, 7\text{MoO}_3$  (para-),  $3\text{M}_2\text{O}, \text{MoO}_3$  (tri-),  $4\text{M}_2\text{O}, \text{MoO}_3$  (tetra- or meta-molybdates),  $8\text{M}_2\text{O}, \text{MoO}_3$ ,  $10\text{M}_2\text{O}, \text{MoO}_3$ , and

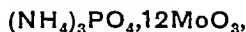


Normal molybdates can be formed only from quite alkaline solutions, so that only the alkali and alkaline-earth metal compounds can be prepared in the wet way; those of other metals can be prepared by fusing requisite quantities of the appropriate oxides. The orange-red mineral *wulfenite* consists of normal lead molybdate, and this salt is sometimes co-precipitated with lead chromate and sulphate to produce lead chrome pigments of modified colour (B.P. 369916; see also Linz, Ind. Eng. Chem. 1939, 31, 298). Ordinary commercial ammonium molybdate consists of the paramolybdate and is crystallised from solutions containing free ammonia. It contains about 5.8% of water of crystallisation, and forms monoclinic prisms.

**Complex Molybdates.**—The well-known yellow ammonium phosphomolybdate precipitated in a nitric acid solution of phosphate by ammonium molybdate (used in the estimation of phosphorus) is but a single example of a large class of complex salts formed from acids derived from molybdic acid and quite a number of other elements: phosphorus, arsenic, boron, silicon, tin, manganese, vanadium, titanium, and others. These heteropolyacids are classified according to the number of  $\text{MoO}_3$  groups associated with each atom of phosphorus or other complex-forming element; this number usually lies between 6 and 12, of which the two limiting values are of most frequent occurrence, particularly 12. Many of these acids are strong acids, and they and their salts frequently exhibit remarkably high solubilities in water and in ether. The structures of the 12-molybdates have been studied by Keggin (J.C.S. 1935,

575) and are based on octahedral  $\text{MoO}_6$  groups, built into rings of three by the sharing of five oxygen atoms, with four such rings arranged tetrahedrally about the central atom (phosphorus or the like). These large anions leave ample space for the appropriate number of relatively small cations and for water of crystallisation. Somewhat similar structures based on molybdenum rings are probable for the other complex molybdates and also for the simple polymolybdates mentioned earlier (see also Pauling, J. Amer. Chem. Soc. 1929, 51, 2868).

**Ammonium Phosphomolybdate**, as precipitated in analysis in presence of ammonium nitrate, always contains some of that salt, together with combined water; on heating for a while at  $180^\circ$  it becomes converted into



in which form it is usually weighed. This compound should contain 3.782% of  $\text{P}_2\text{O}_5$ , but it is found in practical analysis that better results are obtainable by using the empirical value 3.753%. On stronger ignition water and ammonia are lost and  $\text{P}_2\text{O}_5, 24\text{MoO}_3$  remains.

**Permolybdates.**—Molybdates in acid solution give a strong yellow colour with hydrogen peroxide, which cannot be extracted by ether. By using strong solutions of normal potassium molybdate a red unstable permolybdate,  $\text{K}_2\text{MoO}_8$ , can be crystallised. Polymolybdates also react with hydrogen peroxide to form yellow per-salts, some of which are remarkably stable.

**"Molybdenum Blue."**—A very characteristic reaction of molybdates is the development of a strong blue colour under reducing, acid conditions, such as by the action of hydriodic acid, sulphur dioxide, hydrogen sulphide, zinc, or organic matter in presence of light. (The last is sometimes employed as a photographic process, paper soaked in ammonium molybdate being used; fixing is by washing with water, but the image fades in time by oxidation of the blue.) The blue product is also formed during the oxidation of the lower valency states of molybdenum; it readily forms a colloidal dispersion in water, from which it is coagulated by positive colloids. It attaches itself firmly to some fibres, notably silk, and is occasionally used as a dye. Molybdenum blue was once regarded as a molybdenum molybdate, and formulæ such as  $\text{Mo}_2\text{O}_5, \text{MoO}_3$  and



used to represent it; but present views do not go beyond noting that the colour is probably associated with the simultaneous presence of molybdenum in two states of oxidation, the actual proportions of each being left open. In some cases, other acids may also be present in the blue.

#### MOLYBDENUM SULPHIDES.

The principal sulphide is the disulphide,  $\text{MoS}_2$ , which occurs naturally as molybdenite, closely resembling graphite in appearance, and often cleaving like mica. X-Ray data reveal a typical hexagonal layer-lattice. The disulphide has a density between 4.5 and 5.0, and melts at



1,185°, dissociating at higher temperatures into lower sulphides. It is converted on heating in the air or by nitric acid into the trioxide, from which it may be regenerated by heating with sulphur. Molybdenum disulphide behaves as a semi-conductor of electricity, its resistance falling as the applied e.m.f. is increased. It also exhibits a photoelectric effect. In the electric arc, molybdenum disulphide loses sulphur and has been supposed to form  $\text{Mo}_2\text{S}_3$  in steel grey needles, but Montoro (Atti. R. Accad. Lincei, 1929, [vi], 9, 331) showed that the substance formed is a mixture of the disulphide with molybdenum carbide,  $\text{MoC}_2$ , which can be dissolved out by *aqua regia*.

Although molybdates are reduced to colloidal molybdenum blue by hydrogen sulphide in acid solution, prolonged action of this gas leads to the production of a brown insoluble molybdenum trisulphide,  $\text{MoS}_3$ . This sulphide decomposes on heating out of the air into the disulphide and sulphur, and it is soluble in alkali sulphides, forming red thiomolybdates, and in polysulphides to form dark-coloured, perthiomolybdates. Both the thiomolybdates and the perthiomolybdates are crystallisable and yield their corresponding acids in the solid condition on judicious treatment with dilute acid.

#### MOLYBDENUM SULPHATES.

Molybdenum trioxide dissolves in concentrated sulphuric acid, but the only definite compound which can be isolated is  $\text{MoO}_2\text{SO}_4$ , the structure of which is discussed by Nicholls, Sænger and Wardlaw (J.C.S. 1931, 1444). Sulphates of quinquivalent molybdenum are represented only by the two brown double salts,  $4(\text{C}_5\text{H}_6\text{N})_2\text{SO}_4 \cdot 5(\text{MoO}_3)_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{MoO}_2)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , reported by the above workers. In the lower (tervalent) state of oxidation, a clearly defined oxysulphate,  $\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot 5$  (or 6)  $\text{H}_2\text{O}$ , was isolated by electrolytic reduction of a solution of the trioxide in sulphuric acid until it had become vivid green in colour, concentrating *in vacuo*, and precipitating with acetone (Wardlaw, Nicholls, and Sylvester, J.C.S. 1924, 125, 1910). Double sulphates with ammonium, potassium, and rubidium have also been prepared. This oxysulphate is, however, not a true sulphate, because its aqueous solution gives no precipitate with barium chloride solution except after boiling; but it exhibits strong reducing properties.

#### MOLYBDENUM SELENIDES.

Hydrogen selenide precipitates the selenide  $\text{Mo}_2\text{Se}_5$  from acid solutions of molybdates;  $\text{MoSe}_2$  is formed by heating the trioxide with selenium;  $\text{Mo}_2\text{Se}_3$  is formed by the latter reaction in presence of alkali carbonate. By passing hydrogen selenide through strongly alkaline solutions of molybdates, red potassium selenomolybdate and blue ammonium selenomolybdate can be produced. All the selenium compounds formed in the wet way are decomposed by oxygen, which must be excluded when they are being handled.

#### MOLYBDENUM FLUORIDES.

Molybdenum and fluorine react at 60–70° to form  $\text{MoF}_6$ , a white, volatile, crystalline substance, m.p. 17.5°, b.p. 35°, hydrolysed by water to give a blue product. Such lower fluorides as have been reported appear doubtful.

#### MOLYBDENUM CHLORIDES.

The following chlorides have been described:  $\text{MoCl}_5$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_3$ , and  $(\text{MoCl}_2)_3$ . The pentachloride forms in greenish-black crystals, m.p. 194°, b.p. 268°, on heating the metal at dull redness in chlorine. The vapour is dark red, and the substance forms dark-red solutions in inert organic solvents such as benzene and carbon tetrachloride. It combines with dry ether forming a compound which decomposes at 80° to give ethyl chloride. Molybdenum pentachloride reacts with hydroxylic substances in the same manner as phosphorus pentachloride,  $\text{MoOCl}_3$  being formed in the first instance. With alcohol the reaction stops at this point, but with water further hydrolysis occurs, followed by self oxidation and reduction to the trioxide and the tetrachloride.

The tetrachloride,  $\text{MoCl}_4$ , is formed as a vapour when the trichloride is decomposed by heat, and is deposited as a brown powder. It decomposes easily into the pentachloride and trichloride, and reacts violently with water, giving a brown solution.

The trichloride is formed on passing the vapour of the pentachloride, diluted with carbon dioxide or hydrogen, through a moderately heated tube, in which it is deposited as a reddish powder. It is insoluble in cold water, but reacts with boiling water; hydrochloric acid is without action, but sulphuric acid dissolves it to a blue solution which becomes green on heating. In addition to this insoluble anhydrous compound, a red, soluble trihydrate has been prepared by reducing a hydrochloric acid solution of molybdenum trioxide in an electrolytic cell until it was red in colour, evaporating *in vacuo*, and extracting with anhydrous ether saturated with hydrogen chloride. This hydrate is extremely hygroscopic, and is very soluble in water, absolute alcohol, or acetone, giving intensely red solutions with strong reducing properties. Alkalis precipitate a black hydroxide, soluble in acids. If potassium chloride is added to a solution of this chloride, pale red crystals of  $\text{K}_2\text{MoCl}_6 \cdot \text{H}_2\text{O}$  separate on warming (Wardlaw and Wormell, J.C.S. 1927, 1087).

Molybdenum Dichloride—or rather its trimer,  $\text{Mo}_3\text{Cl}_6$ —is formed on heating the trichloride, preferably out of the air, and is distinct from all the other chlorides on account of its non-volatility. It forms a yellow powder insoluble in and unaltered by water, but soluble in alcohol and ether, in which its molecular weight corresponds with the triple formula given above. The salt dissolves in strong hydrochloric acid, and from the solution the hydrates  $\text{Mo}_3\text{Cl}_6 \cdot 3\text{H}_2\text{O}$  and  $\text{Mo}_3\text{Cl}_6 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$  can be crystallised. Molybdenum dichloride is undoubtedly not a simple chloride, but behaves as the chloride of the complex  $[\text{Mo}_3\text{Cl}_4]^{++}$ ; thus sulphuric acid expels only two chlorine atoms as

hydrochloric acid; an alcoholic solution of this chloride reacts with alcoholic silver nitrate solution to form the nitrate,  $(\text{Mo}_3\text{Cl}_4)(\text{NO}_3)_2 \cdot \text{EtOH}$  (the only known nitrate of molybdenum), while from a solution of the dichloride in alkali, acetic acid precipitates the corresponding hydroxide,  $(\text{Mo}_3\text{Cl}_4)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , which forms salts with strong acids, and also shows feebly acidic properties. The configuration of these compounds has been discussed by Lindner (Ber. 1922, 55 [B], 1458).

#### MOLYBDENUM BROMIDES.

The bromides  $\text{Mo}_3\text{Br}_6$ ,  $\text{MoBr}_3$ , and  $\text{MoBr}_4$  are known, and are quite analogous to the corresponding chlorides. The pentabromide is only known in the form of complexes.

#### MOLYBDENUM IODIDES.

Brown  $\text{MoI}_2$  (probably trimeric) has been prepared from molybdenum pentachloride and hydrogen iodide. It is stable up to  $400^\circ$  *in vacuo*, but is oxidised in air or chlorine at  $200^\circ$ . Many mixed halides have been reported.

#### MOLYBDENUM OXY- AND HYDROXY-HALIDES.

Molybdenyl Fluoride,  $\text{MoOF}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , or perhaps a tetrahydrate, is obtained as an insoluble, buff-coloured precipitate by treating the corresponding chloride (see below) with ammonium fluoride (Wardlaw and Wormell, *l.c.*). The fluoride  $\text{MoOF}_3$  has not been isolated, but numerous salts of the types  $5\text{MF} \cdot 3\text{MoOF}_3$  and  $2\text{MF} \cdot \text{MoOF}_3$  have been crystallised from solutions of molybdenum dioxide in hydrofluoric acid to which ammonia or a metal hydroxide has been added.  $\text{MoOF}_4$  is formed from anhydrous hydrogen fluoride and the corresponding chloride, and consists of white crystals, m.p.  $97^\circ$ , b.p.  $180^\circ$ , which dissolve with a hissing sound in water or alcohol, becoming hydrolysed to  $\text{MoO}_2\text{F}_2$ . This compound can also be formed from molybdenum trioxide and hydrofluoric acid; it forms white crystals, subliming at  $265\text{--}270^\circ$ , which are hygroscopic, soluble in water and methyl and ethyl alcohols, but sparingly so in ether, chloroform, or carbon tetrachloride. Derivatives of the last two oxyfluorides — fluomolybdates — of various compositions up to  $\text{MMoOF}_5$  have been prepared by the action of hydrofluoric acid on molybdates.

Molybdenyl Chloride,  $\text{MoOCl}_4 \cdot 4\text{H}_2\text{O}$ , is of interest in that it occurs in two isomeric forms, red and green. Both are produced by electrolytic reduction of solutions of molybdenum trioxide in hydrochloric acid, the particular form produced depending on the concentration of free acid. At the conclusion of the reduction, the solution is concentrated *in vacuo*, and excess of acetone added to precipitate the salt. Wardlaw and collaborators regard these two modifications as *cis*- and *trans*-arrangements of the six co-ordinate linkages, the green form being the *trans*-isomer. Other molybdenyl salts (*i.e.*, salts containing the radical  $\text{MoO}$ ) can be prepared by double decomposition from this chloride; air must be carefully excluded, as oxidation occurs very easily. In solution in water without free acid these salts are slowly hydrolysed. In

presence of potassium chloride the bright yellow  $\text{KMoOCl}_3 \cdot 3\text{H}_2\text{O}$  can be prepared (Wardlaw *et al.*, J.C.S. 1927, 130, 512). As in the case of the fluorides, the quinequivalent oxychloride  $\text{MoOCl}_3$  is unknown, but double salts such as  $2\text{NH}_4\text{Cl} \cdot \text{MoOCl}_3$  can be crystallised from the solution obtained by reducing solutions of the trioxide in hydrochloric acid in presence of ammonium chloride (James and Wardlaw, *ibid.* 1927, 2145). The hydrolysis product,  $\text{Mo}_3\text{O}_4(\text{OH})\text{Cl}$ , can be precipitated from similar reduction products in the absence of ammonium chloride, by precipitating with acetone after concentration *in vacuo*.

The chloride  $\text{MoO}_2\text{Cl}_2$  of molybdic acid may be formed by the chlorination of the dioxide, by heating a mixture of the trioxide and carbon in chlorine, or by judicious oxidation of the pentachloride with oxygen. It sublimes easily without melting, forming thin tetragonal plates; it is readily soluble, with hydrolysis, in water. On heating out of the air this oxychloride is said to pass into violet or dark red needles of  $\text{Mo}_3\text{O}_5\text{Cl}_8$ . Molybdenum trioxide also unites readily with hydrogen chloride to form the hydroxy-oxychloride,  $\text{MoO}(\text{OH})_2\text{Cl}_2$ , which is readily volatile and forms white crystals. This substance is hydrolysed by water, but apparently exists to some extent in solutions of the trioxide in concentrated hydrochloric acid, as it can be extracted from such solutions by shaking with ether, in which it is remarkably soluble. A paste of this substance with concentrated hydrochloric acid solidifies on warming to a mass of pale green prisms or plates, believed to be  $\text{Mo}(\text{OH})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$ . The hydroxy-derivative of the dichloride,



has already been discussed in connection with that chloride. Bromine compounds analogous to most of the foregoing chlorine compounds are known.

#### MOLYBDENUM NITRIDES.

Three nitrides have been reported by Hägg (Z. physikal. Chem. 1930, B, 7, 339); they are formed by heating the metal in an atmosphere of ammonia. The compounds  $\text{MoN}$  and  $\text{Mo}_2\text{N}$  are stable at ordinary temperatures, and the third, probably  $\text{Mo}_5\text{N}_2$ , exists only above  $600^\circ$ .

#### PHOSPHORUS COMPOUNDS OF MOLYBDENUM.

Molybdenum Phosphide, probably  $\text{MoP}_2$ , is formed on heating a mixture of the trioxide, metaphosphoric acid, and carbon to a high temperature.

Molybdenum Phosphates.—Wardlaw and his collaborators prepared an insoluble molybdenyl phosphate from the chloride  $\text{MoOCl}$  by double decomposition; in its higher states of oxidation molybdenum forms the complex phosphomolybdates only, mentioned in connection with molybdic acid.

#### COMPOUNDS OF MOLYBDENUM WITH SILICON AND CARBON.

A silicide,  $\text{MoSi}_2$ , is formed in tetragonal crystals in the electric furnace by direct com-



ination; the only silicates are the complex silicomolybdates. Two highly refractory carbides,  $\text{MoC}$  and  $\text{Mo}_2\text{C}$ , are produced by direct combination at electric-arc temperatures; they are very hard and inert, but can be attacked by fusion with oxidising agents. A carbonyl,  $\text{Mo}(\text{CO})_6$ , is formed from finely divided, freshly reduced metal and carbon monoxide at high pressure ( $200^\circ$  at  $250 \text{ atm.}$ ), but an easier procedure is to conduct carbon monoxide through the product of reaction between molybdenum pentachloride and a Grignard reagent. This carbonyl is a white crystalline solid (rhombic), subliming easily between  $30^\circ$  and  $40^\circ$  and unaffected by air. It is fairly inert, except towards oxidising agents. Carbonates of molybdenum are not known.

**Cyanogen Compounds.**—Quadri- and quinque-valent molybdenum form a series of molybdo- and molybdi-cyanides which bear considerable resemblance to the ferro- and ferricyanides, although the molybdenum atom coordinates eight cyanogen groups. Potassium molybdocyanide,  $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ , may be prepared by the action of reducing agents (e.g., hydrogen sulphide) on a solution of potassium molybdate and potassium cyanide, and forms yellow orthorhombic crystals. Partial hydrolysis occurs in alkaline solutions of this salt, from which the red salt  $\text{K}_4[\text{Mo}(\text{OH})_4(\text{CN})_4] \cdot 6\text{H}_2\text{O}$  can be crystallised. Further hydrolysis gives  $\text{K}_3[\text{Mo}(\text{CN})_4(\text{OH})_3]$  and  $\text{K}_2[\text{Mo}(\text{CN})_4(\text{OH})_2]$  (blue), of which the latter is converted by dilute acid into the basic cyanide  $\text{Mo}(\text{CN})_2(\text{OH})_2$ . Oxidation of molybdocyanides by potassium permanganate and similar reagents yields molybdicyanides, e.g.,  $\text{K}_3[\text{Mo}(\text{CN})_8]$ . Double (or more complex) cyanides of tervalent molybdenum are also known.

#### COMPOUNDS OF MOLYBDENUM AND BORON.

The boride,  $\text{Mo}_3\text{B}_4$ , is said to be formed from the elements in the electric furnace, but doubt exists as to its exact composition. It has been reported to be extremely hard and chemically inert. The only borates appear to be the complexes with molybdic acid.

G. H. C.

**MOLYBDENUM, ANALYTICAL CHEMISTRY OF.** Qualitative.—In the course of systematic qualitative analysis, molybdenum is precipitated from acid solutions by hydrogen sulphide, and its sulphide is soluble in sodium or ammonium sulphide solution along with those of arsenic, antimony, and tin. The mixed sulphides precipitated by acidification of the solution are dissolved in *aqua regia*, and the resulting solution, after addition of excess of ferric chloride, precipitated with ammonia. The filtrate contains ammonium molybdate, which is identified as follows:

(a) On acidification with acetic acid the solution gives an orange to yellow coloration with tannin solution, due to the red molybdenum tannin complex, which can be flocculated by addition of a large excess of ammonium chloride to the hot solution.

(b) The hot molybdate solution gives with lead acetate a white to cream-coloured precipi-

tate of lead molybdate, which, after filtration, may be identified as such by heating with a few drops of strong sulphuric acid until this is almost completely volatilised; on cooling, the liquid turns deep blue. Powdered molybdenum minerals give the same reaction when heated with sulphuric acid.

(c) The solution of ammonium molybdate, when treated with nitric acid, ammonium nitrate, and a few drops of phosphate solution, yields the characteristic yellow crystalline precipitate of ammonium phosphomolybdate.

Alkaline solutions obtained after fusion of minerals, etc., with alkaline oxidising fluxes may contain molybdate, possibly with tungstate, vanadate, phosphate, arsenate, etc. Molybdenum is recovered by addition of sodium tartrate and sulphide, and acidification of the hot solution. The sulphide precipitate is dissolved in *aqua regia* and the molybdate solution tested as described above.

The most sensitive test for molybdenum (in the form of molybdate) consists in acidifying the solution with a mineral acid and adding potassium ethyl xanthate. In presence of  $0.0006 \text{ mg.}$  per ml. or more of molybdenum, a plum-red coloration is formed, and this can be extracted with an organic solvent (e.g., ether 65 and light petroleum 35%). For this and other tests, see W. R. Schoeller and A. R. Powell, "The Analysis of Minerals and Ores of the Rarer Elements," 2nd ed., London, 1910, p. 200.

**Quantitative. Separation.**—Molybdenum may be separated as sulphide from all metals not precipitated by hydrogen sulphide from acid solutions. If the amount of molybdenum to be precipitated exceeds a few centigrams, its precipitation may be incomplete owing to reduction, the solution turning light blue. In such a case the precipitate should be filtered off, the filtrate boiled free from hydrogen sulphide, oxidised by boiling with persulphate, and the treatment with hydrogen sulphide repeated. Precipitation with hydrogen sulphide under pressure is ineffective, and is not recommended.

The separation from tungsten and vanadium is effected by precipitation of molybdenum as sulphide from a solution containing sufficient tartaric acid to prevent co-precipitation of the two elements. Tungstic acid precipitated by the usual acid treatment occludes molybdenum; it should be dissolved in ammoniacal tartrate solution, and the liquid tested with hydrogen sulphide after acidification. The quantitative separation of arsenic is effected by distillation. Small amounts of vanadium, as well as arsenic, antimony, tin, bismuth, and phosphorus, can be eliminated from molybdate solutions by precipitation on ferric hydroxide; iron and copper may be precipitated as hydroxides by means of caustic soda, and calcium by sodium carbonate. All these separation processes, as well as the gravimetric and volumetric methods given below, are fully described by W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," New York, 1929, pp. 246-256, and by W. R. Schoeller and A. R. Powell (*op. cit.*).

**Determination. Gravimetric.**—The most re-

liable and convenient method for the gravimetric determination of molybdenum consists in its precipitation as lead molybdate, which should always be applied in preference to ignition of molybdenum sulphide to the trioxide. The latter operation must be conducted with care at a temperature not greatly exceeding 500°C. to avoid volatilisation losses. Precipitation as lead molybdate also separates molybdenum from the bivalent metals copper, cobalt, nickel, manganese, zinc, and magnesium.

**Volumetric.**—For the volumetric determination, Hillebrand and Lundell (*op. cit.*) recommend, as a reliable method, the reduction of the molybdate solution to the sesquioxide state in a Jones reductor, collection of the reduced solution in one of ferric sulphate, and titration of the reduced iron.

For *colorimetric* determination, see **CHEMICAL ANALYSIS**, Vol. II, 672; Elder, *Analyst*, 1943, 68, 14.

W. R. S. and D. A. L.

### MOLYBDENUM MINERALS.

Although several molybdenum minerals are known, the only one of commercial importance is the sulphide, *molybdenite*,  $\text{MoS}_2$ , which provides practically all the world's supply of molybdenum. The orange-yellow lead molybdate, *wulfenite*,  $\text{PbMoO}_4$ , which is occasionally found in the oxidised parts of certain lead-molybdenum veins, was formerly the main source of molybdenum, but is now obtained only in relatively small amounts from the Mammoth mines in Arizona. From molybdenite the hydrous ferric molybdate, *molybdic ochre*, is formed by surface alteration; it may serve rarely as a minor contributory source of molybdenum.

The world production of molybdenum in 1940 is estimated at approximately 16,000 tons, of which the United States yielded 92%, Norway and Mexico about 2% each, and Peru 1%. In the decade prior to 1940 the molybdenite-bearing quartz veins at Climax, Colorado, provided more than 80% of the entire world output of molybdenum. Since 1940, however, about 30% of the molybdenum produced in the United States has been derived as a by-product from the treatment of copper ores in Utah and New Mexico. By-product molybdenite is also being concentrated from the copper ores of Kounrad in Soviet Asia, of Braden in Chile, and elsewhere.

For a brief statement on the uses of molybdenum, and selected references to the literature, see **MOLYBDENUM** (this Vol., p. 220a).

D. W.

### MOLYBDITE or MOLYBDIC-OCBRE.

This mineral, formerly considered to be molybdenum trioxide,  $\text{MoO}_3$ , is really a hydrated ferric molybdate,  $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ . On account of its iron content the mineral is often referred to as *ferrimolybdate*. It occurs sparingly as yellowish powdery encrustations or fibrous tufts formed by the oxidation of molybdenite, and in exceptional cases it is a minor contributory source of molybdenum in the upper parts of molybdenite deposits. The existence of molybdic oxide as a natural mineral has not been established.

D. W.

**MOMENTS, ELECTRIC DIPOLE.** The *electric dipole moment* of a substance is a measure of its electrical asymmetry. Since electrical asymmetry and structural asymmetry are often related, measurements of this quantity have been extensively used to elucidate problems of stereochemistry. The quantity is a characteristic of a substance and may have very different values for substances which in other properties are very similar. It therefore has possible uses in analysis or for following the course of reactions.

The electric dipole moment is a very important physical concept in the theory of dielectrics, not only of the dielectric constant but also of dielectric loss—subjects of great industrial importance.

### THEORY.

In a uniform field, since all the forces on the negative charges associated with a molecule are parallel, it may be said that these charges have a negative centroid (like a centre of gravity). There is similarly a positive centroid. The forces acting through these centroids must be opposed and, if the molecule as a whole is electrically neutral, they must be equal, *i.e.*, the molecule as a whole is subjected to a couple which is determined by the field strength, by the orientation of the molecule in the field, and by the product of total charge (*i.e.*, the sum of the atomic numbers) and the distance between the centroids, *l*. This product,  $\mu$ , is a moment; it is called the *electric dipole moment* of the molecule. It may readily be seen that while molecules in general have non-zero moments, it is possible that in some of high symmetry the centroids will coincide and the moment be zero. The moment is defined not only by its magnitude, *i.e.*, the product of the charge at one centroid and the distance between the centroids, but by the direction of the line joining the centroids; it is, therefore, a vector. If the molecule has an axis of symmetry, the vector must lie along the axis; a molecule with more than one such axis must therefore be non-polar. Similarly, if it has a plane of symmetry, the vector must lie in the plane; a molecule with three such planes, or with an axis of symmetry perpendicular to a plane, is therefore non-polar. These rules cover many, but not all, the cases of non-polarity.

Since the moment of the whole molecule is a vector, it may be regarded as the vector sum of moments characteristic of individual bonds or of groups. This is a very useful conception. The final decision as to whether or not a molecule should be non-polar is reached by compounding these group or bond moments and seeing whether the resultant vanishes. Sometimes, as in the case of the higher paraffins, a molecule which has no spatial symmetry and which contains bonds which are probably polar, nevertheless proves to be non-polar as a whole.

The vector character of bonds may be illustrated by the dipole moments of a number of chlorine derivatives of hydrocarbons, shown in Table I.

The values are expressed in Debye units (*see below*). These values agree qualitatively, though not quantitatively, with the predictions based

on the vector picture. Thus, while only *trans*-dichloroethylene, *p*-dichlorobenzene, and carbon tetrachloride are non-polar, the moments of methyl chloride and chloroform are not equal,

TABLE I.

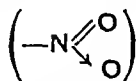
Substance.	$\mu$ in D.
(Vinyl chloride . . . . .)	1.44)
<i>cis</i> -Dichloroethylene . . . . .	1.74
<i>trans</i> - " . . . . .	0
(Chlorobenzene . . . . .)	1.56)
<i>o</i> -Dichlorobenzene . . . . .	2.33
<i>m</i> - " . . . . .	1.48
<i>p</i> - " . . . . .	0
Methyl chloride . . . . .	1.86
Methylene dichloride . . . . .	1.59
Chloroform . . . . .	1.48
Carbon tetrachloride . . . . .	0

nor are those of chlorobenzene and *m*-dichlorobenzene, and the moment of *o*-dichlorobenzene is not  $\sqrt{3}$  times that of chlorobenzene (2.70). These deviations are due to alteration of each dipole by the field of the other, *i.e.*, by induction.

By resolving the resultant moment for a molecule of known geometry, or by considering



means whereby the direction of the dipole of one group can be determined absolutely, the direction of others may be determined by this method of measuring the moment of the appropriate *p*-disubstituted compound and seeing whether the value is nearer the arithmetical sum or difference of the component moments. The nitro-group can be taken as an absolute basis, because the co-ordinate link from nitrogen to oxygen which it contains



must certainly confer a negative charge on the oxygen end of the group, *i.e.*, the end further from the aryl group.

Although direct inductive effects are very small in *p*-disubstituted benzene compounds, marked departures from additivity are sometimes found which are not explicable except on the basis of valency changes arising because of the conjugated nature of the bond system. Thus *p*-nitroaniline has a moment of 6.10 D., which is 0.62 D. greater than the highest possible theoretical value of 5.48 D., the arithmetical sum of the moments of nitrobenzene and aniline. The existence of the inductive and the conjugation effects complicates the use of electric dipole moments for precise investigations of geometrical structure, but, on the other hand, they make it possible to use the measurements to detect certain kinds of valency change.

#### MEASUREMENT.

The electric dipole moment of a molecule is determined from measurements of the dielectric constant of the vapour of the substance or of its dilute solutions in non-polar solvents such as benzene, carbon tetrachloride, *n*-hexane, cyclohexane, or 1:4-dioxane. The dielectric constant

simple molecules containing only one markedly polar bond or group, it is possible to obtain component moments of these bonds or groups; but from the foregoing it will be realised that such values are only of limited usefulness. When the polar groups are more than 3 Å. apart they have little direct inductive effect on each other; therefore some *p*-disubstituted benzene compounds show good additivity (*see* Table II).

TABLE II.

Values of Dipole Moments in D.

Toluene	0.4.	Chlorobenzene	1.56.	Nitrobenzene	3.95.
<i>p</i> -Chlorotoluene	. . . . .	1.95	(1.06)		
<i>p</i> -Nitrotoluene	. . . . .	4.44	(4.35)		
<i>p</i> -Chloronitrobenzene	. . . . .	2.57	(2.39)		

The values in parentheses are those calculated by simple scalar algebraic addition, on the supposition that the nitro-group and chlorine atom have the negative poles of their dipoles away from the benzene ring, while the methyl group has the positive pole farther from the ring (*see below*). It is clear that, provided there is some

is a function of the dipole moment because the polar molecules orient in the electric field between the plates of a condenser, under the action of the couple (*vide supra*), and so change the effective charges on the plates. For a gas or vapour the relation between the dipole moment,  $\mu$ , and the macroscopic properties is given by the equation:

$$\{(\epsilon-1)/(\epsilon+2)\}(M/\rho) = 4\pi N\{\alpha + (\mu^2/3kT)\}/3 = P \dots (1)$$

where  $\epsilon$  is the dielectric constant,  $M$  the molecular weight,  $\rho$  the density,  $N$  the Avogadro number,  $k$  the Boltzmann constant, and  $T$  the absolute temperature.  $\alpha$  is a measure of the ease with which the molecule may be deformed electrically in the field, and  $P$  is termed the molecular polarisability—it has the dimensions of volume and is expressed in c.c.

Putting

$$P = [R] + A/T \dots (2)$$

where  $[R] = 4\pi N\alpha/3$  and is the molecular refractivity (*see below*), and  $A = 4\pi N\mu^2/9k$ , by measuring  $P$  at a series of temperatures and plotting the results against  $1/T$ ,  $\mu$  can be determined from the slope of the linear graph thus obtained.

For a mixture of gases containing mol. fractions  $x_1$  and  $x_2$  of two components having moments  $\mu_1$  and  $\mu_2$  and molecular weights  $M_1$  and  $M_2$ , the relation is:

$$\{(\epsilon-1)(\epsilon+2)\}((M_1x_1 + M_2x_2)/\rho) = P_1x_1 + P_2x_2 = P_{1,2} \dots (3)$$

where  $P_1 = 4\pi N\{\alpha_1 + (\mu_1^2/3kT)\}/3$

and  $P_2 = 4\pi N\{\alpha_2 + (\mu_2^2/3kT)\}/3$ .

It will be noticed that the effect on the dielectric constant  $\epsilon$  of the mixture is a function of the square of the dipole moment. A small

proportion of a component with a large dipole moment would therefore have a marked effect upon  $P_{1,2}$ .

For a mixture of liquids the same relation holds within limits. It is true if both components are non-polar or if one is non-polar (component 1) and one (component 2) weakly polar ( $\mu > 1.5$  D.): when the second component is more polar it is assumed to be true only in the limit when  $x_2 \rightarrow 0$ . Therefore the common practice is to evaluate  $P_2$  at infinite dilution. This may be done either by assuming that  $P_1$  is the same when  $x_2$  is small, as for pure component 1 (when  $x_2=0$ ), or by drawing the tangent at  $x_2=0$  to the curve of  $P_{1,2}$  against  $x_2$ , which procedure, since  $dP_{1,2}/dx_2 = P_2 - P_1$ , gives  $P_2$  if  $P_1$  is known in the limit  $x_2 \rightarrow 0$ . The molecular polarisation, and therefore the dipole moment, which is found to apply in solution for a polar component is, however, usually different from that found for the same substance in the vapour phase. This solvent effect is a complicated function of the dielectric constant of the solvent and of the shapes of the solvent and solute molecules; one solvent does not have the same effect upon the moments of all solutes. Furthermore, the solvent effect varies with temperature because of its dependence on the dielectric constant of the solvent; it is not possible, therefore, to obtain a moment in solution from the temperature variation of the molecular polarisability. There is, however, a quite different method which has been very extensively applied to solution measurements.

As was mentioned previously, the quantity  $4\pi Na/3$ , or  $[R]$ , is the molecular refractivity. At the very high frequency of the alternating electric field accompanying a visible light wave the dipoles cannot orient; the molecular polarisability at these frequencies would therefore contain no dipole term. In practice it is impossible to measure dielectric constants at such high frequencies, but Maxwell showed that if this quantity and the refractive index,  $n$ , could be measured at the same field frequency, then  $n^2 = \epsilon$ , and the equation may be written

$$[R] = 4\pi Na/3 = \{(n^2 - 1)/(n^2 + 2)\} \{M/\rho\} \quad (4)$$

whence  $[R]$  is called the molecular refractivity.

Hence, by measuring the dielectric constant in fields of relatively low frequency ( $10^7$  or less), the refractive index for visible light (usually the sodium doublet or the mercury green line), and the density, all at a known temperature, the moment may be evaluated from equation (2) rearranged thus:

$$A/T = P - [R]$$

the dielectric constant giving  $P$  and the refractive index  $[R]$ .

For a solution of a polar solute in a non-polar solvent the following relation corresponds to equation (3):

$$\begin{aligned} &\{(n^2 - 1)/(n^2 + 2)\} \{(M_1 x_1 + M_2 x_2)/\rho\} \\ &= [R_1] x_1 + [R_2] x_2 = [R_{1,2}] \quad \dots (5) \end{aligned}$$

therefore  $[R_2]$ , the molecular refractivity of the solute, can readily be obtained from the refractivities of solution and pure solvent. The method can therefore be applied very readily to

the determination of dipole moments in solution.

These methods, especially the second, are those which have been used for nearly all measurements of moments; there are others but they are of little practical importance. The methods described give practically identical results when applied to gases or vapours; both give values affected by the solvent when applied to solutions, but whereas the value from the "refractivity" method is to be regarded as a normal moment with a solvent-effect moment superimposed, the value from the "temperature" method is doubly complicated, owing to the variation of the solvent effect with temperature, and therefore is of no practical significance.

Electric dipole moments are expressed in *Debye units* (represented D.); 1 D. is equivalent to  $10^{-18}$  C.G.S. unit, being the product of a distance of 1 Angstrom unit ( $10^{-8}$  cm.) and an electric charge of  $10^{-10}$  of an electrostatic unit.

#### RESULTS AND INDUSTRIAL APPLICATIONS.

The electric dipole moments of a considerable number of substances, organic and inorganic, have been measured in the vapour phase; the number measured in solution is well over one thousand and includes most of the commoner inorganic and organic substances which are fairly soluble in the non-polar solvents listed in the previous section. These data are available in the following compilations:

Transactions of the Faraday Society, 1934, Appendix, "A Table of Dipole Moments."

Tables Annuelles de Constantes et Données Numériques, "Constantes Diélectriques, Moments Électriques," Paris, 1937.

Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Berlin, 5te Auflage; 2te Ergänzungsband (i) (1931), pp. 74-86; 2te Egb. (ii) (1931), pp. 969-1016; 3te Egb. (i) (1935), pp. 117-152.

The applications to chemical problems have been discussed in the following monographs:

P. Debye, "Polar Molecules," New York, 1929. *Idem*, "The Dipole Moment and Chemical Structure," London, 1931.

C. P. Smyth, "Dielectric Constant and Molecular Structure," New York, 1931.

J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford, 1932.

N. V. Sidgwick, "The Covalent Link in Chemistry," New York, 1933.

R. J. W. Le Fèvre, "Dipole Moments," London, 1938.

There are also articles in such recent advanced text-books as S. Glasstone, "Text Book of Physical Chemistry," London, 1940. Review articles have appeared in the Annual Reports of the Chemical Society for 1931, 1935, 1936, and 1940; and in Chemical Reviews for 1936, 19, 1939, 25, and 1942, 30.

The Faraday Society held a Discussion reported in Trans. Faraday Soc. 1934, 30, 677 *et seq.*

The measurements can be of great value when problems of molecular structure arise. Alternative structures which differ in symmetry can often be readily distinguished, *e.g.*, *trans* struc-

tures may be distinguished from *cis*, or *para* disubstituted benzene compounds from *ortho* or *meta*, provided that the possibilities of rotation of groups about single bonds, which may produce great changes in symmetry, do not cause complications. Examples of compounds the structures of which have been thus studied are ethylene derivatives, oximes, and diazocyanides. For such applications it is immaterial that measurements in solution do not give a true value of the moment. The apparent moment of a polar group forming part of a molecule is reasonably constant in one solvent at a definite temperature, and if it is known in a given environment this is all that is necessary for solving problems the essence of which is the orientation of one such group relative to another. More elaborate applications to problems of geometrical arrangement of structures are possible and are discussed in the works cited.

Electric dipole moments could be employed in the identification of compounds, preferably when the choice of possibilities lies between a few compounds differing considerably in moment. The values for most compounds are between 1 and 4 D., and the usual accuracy of determination is not better than  $\pm 0.01$  D.; the moment alone is not, therefore, likely to be an adequate means of identification, but it can be a useful adjunct.

As a means of establishing purity the dipole moment could be very useful in particular cases where the compound proper is non-polar or has only a small moment, say not greater than 1.5 D., but the possible impurities are highly polar. This is because of the fact, previously remarked upon, that the effect on the polarisation of the mixture is a function of the squares of the moments of the components [equation (3)].

The dipole moment can be used for following the course of a simple reaction, as was done for example in the case of the conversion of the *cis*-to the *trans*-diazocyanides (Le Fèvre and Vine, J.C.S. 1938, 431) or for analysing the equilibrium mixture of two simple substances, one polar and the other non-polar, as was done for *cis*- and *trans*-azobenzenes (Hartley and Le Fèvre, *ibid.* 1939, 531).

Since the molecular polarisation of a mixture is a weighted mean of those of the constituents, it is clear that from one measurement on a mixture it is possible only to determine the proportions of two substances of known moment; if there are more than two substances, one of them must somehow be removed and another measurement then made.

A very important use of electric dipole moments in pure chemistry has been in elucidating fundamental questions of electronic structure and of reactivity; this may not be directly applicable to technical processes, but anything which advances the general understanding of a subject is of indirect value in industrial problems. The matter is discussed in the later of the works cited.

Since dipole moments have to be evaluated by calculations involving the density as well as the dielectric constant and refractive index, determinations cannot be made instantaneously; but in suitable circumstances, e.g., in controlling

the composition of a binary liquid mixture, the dielectric constant alone can be employed. It can give an instantaneous and continuous indication of composition; and provision could readily be made for an audible or visible warning to be given if the composition deviated from a pre-determined standard. The same property could be used to control any one of the three variables composition, pressure, or temperature of a gas stream when the other two are constant.

If a heterodyne apparatus were employed (see monographs cited above) the presence of a polar impurity in a gas stream could be detected by passing the stream through the condenser of one oscillator and then, after passage through an absorbent, through the condenser of the other oscillator.

Such applications have been discussed by various authors (Chrétien and Laurent, *Compt. rend.* 1932, 195, 792; Henriquez, *Rec. trav. chim.* 1935, 54, 327; Henriquez and Van der Hulst, *Chem. Weekblad*, 1935, 32, 35; Ebert, *Angew. Chem.* 1934, 47, 305; Tansz and Rumm, *Kolloid-Beih.* 1933, 39, 58; Müller, *Ind. Eng. Chem. [Anal.]*, 1941, 13, 741), but the only one which has been made at all extensively is the determination of the moisture content of porous materials. The field awaits fuller commercial exploitation.

The importance of the electric dipole moment in the theory of dielectrics was indicated in the introduction. A survey of the fundamental principles and of recent developments has been given by Moullin (*J. Inst. Elec. Eng.* 1940, 88, 113).

## APPENDIX.

### COMMERCIAL INSTRUMENTS FOR THE DETERMINATION OF MOISTURE CONTENT IN POROUS SOLIDS.

As will be readily appreciated from the foregoing, water absorbed by a porous material has a marked effect on the dielectric constant. This principle is used in two instruments intended for moisture content determination of such materials in granular or powder form.

One, made by the Cambridge Instrument Company, Ltd., utilises a high-frequency circuit (Catalogue No. 23661). The other, designed at the National Physical Laboratory and made by the Baldwin Instrument Company, Ltd., works at alternating electric mains frequency (see "The N.P.L. Moisture Meter," L. Hartshorn and J. D. Mounfield, *Milling*, January 8, 1944). In both instruments the material to be tested is poured into a cup, which forms a condenser, and the alternating current therein is rectified and passed through a milliammeter. This can be calibrated in terms of moisture content for the particular material under test by using samples in which the content is determined initially by whatever standard method is commonly used. Determinations are many times quicker than by ordinary methods, and the accuracy is fully adequate for most purposes.

L. E. S.

MOMENTUM, ANGULAR (v. this Vol., p. 188c).

**MOMORDICA FAT.** *Balsam pear-seed oil.* *Balsam apple-seed oil.* The *Momordicaceæ* (Fam. Cucurbitaceæ) are a genus of tropical climbing plants with orange or red fleshy fruits. Toyama and Tsuchiya (*Amer. Chem. Abstr.* 1936, 30, 7372) extracted 40.9% of oil from the kernels of *Momordica charantia* and recorded the following data:  $\rho_4^{40}$  0.9153,  $n_D^{40}$  1.5010, m.p. 26–27°, acid value 0.63, sap. value 189.9, iodine value (Wijs) 140, unsaponifiable 0.91% (cf.

Corfield and Caird, Pharm. J. 1920, 104, 43). Toyama and Uozaki (A. 1937, III, 445) found  $\alpha$ -elaostearic acid in the oil of *M. cochinchinensis*. From this plant Kuwada and Yosiki (Amer. Chem. Abstr. 1937, 31, 8542; 1940, 34, 5088; 1941, 35, 461) isolated the sterol "bessisterol"  $C_{29}H_{48}O$ ,  $0.5H_2O$  which proved to be identical with spinasterol. Corfield and Grant (*l.c.*) consider that the oil could be used in the manufacture of paint.

**MONARDÆIN** is identical with *salvianin* (v. Vol. VI., 92a).

**MONALIN** is identical with *pelargonin* (v. Vol. VI., 93a) (Robinson and Todd, J.C.S. 1932, 2488; Karrer and Widmer, Helv. Chim. Acta, 1927, 10, 67, 729).

**MONASCIN**. The so-called red rice, which is met with in Eastern Asia, results from the growth on the rice of a fungus, *Monascus purpureus*, Went (Fam. Monascaceæ. It contains a red colouring matter which is said to be used in China for colouring beverages and eatables.

By extracting "red" rice with ether two pigments can be isolated, a deep brown-red substance which has not yet been obtained pure, and a deep yellow compound, termed *monascin* (Salomon and Karrer, Helv. Chim. Acta, 1931, 14, 18; Karrer and Geiger, *ibid.* 1941, 24, 289).

*Monascin*,  $C_{20}H_{24}O_5$  or  $C_{20}H_{26}O_5$ , deep yellow leaves, m.p.  $141-142^\circ$ , is insoluble in water and contains no methoxyl group. One active hydrogen atom is present (Zerewitinov) but this is not part of a hydroxyl group since monascin cannot be acetylated or benzoylated. Monascin contains at least three methyl groups attached to carbon, and on ozonisation forms an ozonide which gives acetaldehyde and pyruvaldehyde when decomposed with water, indicating the presence of  $CHMe$ : and  $:CMe:CH$ -, the latter probably existing in an isoprene residue. Reduction with zinc dust converts monascin into the colourless *dihydro-monascin*, decomposing above  $162^\circ$ , whilst by catalytic reduction four molecules of hydrogen are added with formation of the non-crystalline *perhydromonascin*. Oxidation of monascin or perhydromonascin with potassium permanganate yields *n*-hexoic acid.

Monascin appears to possess a chromophoric system analogous to those of bixin, crocetin, and rhodoxanthin. It possibly contains one enolic hydroxyl group, whilst at least two of the oxygen atoms are present in carbonyl groups.

Nishikawa (J. Agric. Chem. Soc. Japan, 1932, 8, 1007) isolated from *Monascus purpureus* a substance termed *monascorubrin*,  $C_{22}H_{24}O_8$ , red needles or prisms, m.p.  $136^\circ$ , which does not contain a methoxyl group and is reduced in presence of a catalyst to the *dihydro*-derivative, both compounds being levorotatory. Oxidation of monascorubrin gives *monascoflavin*,  $C_{17}H_{22}O_4$ , yellow rhombic platelets, m.p.  $145^\circ$ , which on catalytic reduction forms a *dihydro*-compound possessing phenolic properties. Both these compounds are dextrorotatory. *n*-Hexoic acid is produced by fusing monascorubrin with potash.

It is concluded, therefore, that monascorubrin contains a double bond, a straight chain of six carbon atoms, and probably a benzene nucleus.

E. J. C.

**MONAZITE**. A mineral consisting of phosphate of the rare-earth metals, essentially  $(Ce, La, Nd, Pr)PO_4$ , usually with some thorium silicate,  $ThSiO_4$ . The thorium content generally ranges from 1 to about 18%. An average of several analyses of commercial monazite is  $Ce_2O_3$  30,  $La_2O_3$ , etc., 30,  $P_2O_5$  26,  $ThO_2$  8,  $Y_2O_3$ , etc., 1.5, and  $SiO_2$  1.3%. It crystallises in the monoclinic system, but well-formed crystals are rare and mostly small, and often occur as tablets flattened parallel to the orthopinacoid. Monazite is usually found in granular masses, and commonly as beach and river sands. It possesses a good parting parallel to the basal plane, has a hardness of  $5\frac{1}{2}$ , and  $\rho$  4.9-5.3. Crystals or masses within pegmatite veins are generally yellowish-brown or reddish-brown and almost opaque, but the rounded grains found in beach deposits are translucent and have honey-yellow and brown tints, and a resinous lustre. Monazite sand can be cracked easily between the teeth. A ready method of identification is by means of a direct-vision pocket spectroscope or an eyepiece spectroscopic attachment to the microscope, in which the characteristic absorption spectra of neodymium and praseodymium can be seen.

Monazite is a comparatively rare mineral found in some granites and associated pegmatites, and in certain gneisses. Such occurrences are not rich enough to be exploited, but since the mineral is extremely resistant to decomposition and weathering it becomes concentrated in river and beach sands, together with other resistant and heavy minerals such as zircon, rutile, magnetite, and ilmenite. The world production of monazite in 1938 was about 6,000 tons, nearly 90% of which came from the beach sands of Travancore in Southern India, the remainder coming largely from sands in Brazil, the Netherlands East Indies, and New South Wales.

Monazite is the chief source of thorium and cerium, and also of lanthanum, neodymium, praseodymium, and the radioactive element, mesothorium. Much of the thorium extracted from monazite is used in the preparation of thorium nitrate for the manufacture of incandescent gas mantles, which consist of 99% of thorium and 1% of ceria. Thorium is a super-refractory employed in crucibles for melting pure metals at temperatures up to  $2,300^\circ C$ ., and is probably the most refractory oxide known. Metallic thorium is alloyed with tungsten in ductile filaments and electron-discharge devices. The use of thorium in photoelectric cells, glow-tubes, electrodes, and X-ray targets is increasing, and there is little doubt that the radioactive properties of the metal will find greater service in the future. Mesothorium, which is normally present in monazite to the extent of about 3 mg. per ton, is a very valuable by-product, since it is approximately 30 times as radioactive as radium. It is used in the treatment of cancer and malignant skin diseases, and as an



ingredient of luminous paints. Cerium is widely used in making ferrocerium, or pyrophoric alloy ("mischmetall"), consisting of about 70% of cerium and 30% of iron, for the manufacture of "flints" for cigarette lighters, etc. Because of its affinity for oxygen, cerium acts as a reducing agent in the production of metallic zirconium and thorium, and the metal has recently been used in some light alloys. The sulphate is employed in making aniline black and in rectifying over-developed negatives in photography, whilst other cerium salts find limited service in medicine, ceramics, optical glassware, dyeing, and tanning. Considerable quantities of cerium fluoride are utilised in making electrodes for electric arc lamps and searchlights. Besides being used with cerium in pyrophoric alloys and flaming carbons, lanthanum and neodymium are in some demand in the textile industry, as preservatives, and in glass and ceramics as colorisers, decolorisers, and opacifiers, whilst lanthanum oxide is also used as a catalyst and as a weighing agent for silk.

*References.*—R. B. Ladoo, "Non-metallic Minerals," New York, 1925, p. 392; F. L. Hess, in "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, New York, 1937, Chap. XXX; L. L. Fernald, "Monazite," Rec. Geol. Survey India, 1935, 70, 260; S. I. Levy, "The Rare Earths, Their Occurrence, Chemistry, and Technology," London, 1915.

D. W.

# MOND GAS (v. Vol. V, 376a).

"MONEL." "Monel" is a nickel-copper alloy produced from ore mined in the Sudbury district of Ontario, Canada. The ore, which is fairly uniform in character, is smelted without separation of the constituent metals, the composition being controlled to fall within a predetermined range. Nominal compositions of the standard grades, all of which are marketed under this registered trademark, are given in Table I.

TABLE I.—CHEMICAL COMPOSITIONS.

Metal.	Ni.*	Cu.	Fe.	Mn.	Si.	C.	S.	Al.
Rolled Products.								
"Monel"	67	30	1.4	1.0	0.1	0.15	0.01	
"K Monel"	67	29	0.9	0.4	0.50	0.15	0.005	2.75
Castings								
"Monel"	67	29	1.5	0.9	1.25	0.3	0.015	

\* Includes small percentage of Co.

The compositions are designed to provide various combinations of properties. Most uses depend upon the combination of one or more of the mechanical properties with corrosion resistance.

## METALLOGRAPHY.

The internal structure of "Monel" is simple and homogeneous. Annealed and hot-rolled material consists of polygonal grains of the nickel-copper solid solution. Castings have the typical cored structure of single solid solutions.

## MANUFACTURE.

Smelting practice follows that applicable to nickel-copper ores for the production of elec-

trolytic nickel, but final separation of the main elements is not carried out. After separation of the sulphide ore from rock and gangue by flotation, it is smelted and roasted to mixed oxides of copper and nickel. These mixed oxides are heated together with carbon to reduce them to metal, the carbon content of which is then adjusted and the metal deoxidised with suitable deoxidants including manganese and magnesium. Ferromanganese may be used if it is necessary to increase the iron content. Deoxidation is carried out in the furnace.

The forging and rolling temperature range for ingots is 1,175–1,010°C. The "hot-short" range, within which forging is not possible, is 870–650°C. The best bending range is 1,230–1,040°C. As far as possible, reduction is carried out by hot rolling; cold working is confined to the production of sheet, wire, strip, and rod, or is used to provide higher strength or other special properties. Bright annealing, which is advantageous in the final stages of manufacture, is standard practice. Freedom from oxidation is secured by a protective atmosphere or by box or pack annealing. The temperature for close annealing is 760°C.; this temperature should be maintained for 2–6 hours. Shorter times and higher temperatures (up to 900°C.) are used for open annealing or in continuous furnaces.

## PHYSICAL PROPERTIES.

*Density.*—The value for the alloy containing 68.5% of nickel is 8.80 (0.318 lb. per cu. in.).

*Change of State.*—The melting-point varies in the range 1,300–1,350°C. The magnetic transformation to the non-magnetic form occurs when the temperature rises above 95°C. The transition temperature is lowered by increase in copper content.

*Specific Heat.*—The specific heat is 0.127 g.-cal. per g. per °C. between 20 and 400°C. The latent heat of fusion is 68 g.-cal. per g.

*Thermal Expansivity.*—The mean coefficient of thermal expansion between 25 and 100°C. is 0.000014; between 25 and 600°C. it is 0.000016.

*Thermal Conductivity.*—The thermal conductivity is 0.06 g.-cal. per c.c. per sec. per °C. in the range 0–100°C.

*Electrical Resistivity.*—The average value of drawn wire is 42.5 microhm.-cm. or 256 ohm.-mil-foot with a temperature coefficient of resistivity at 20°C. of 0.0019 per °C. The value rises to 72.5 microhm.-cm. at 1,000°C. The alloy is not used for electrical resistance purposes.

*Magnetic Properties.*—The alloy is weakly magnetic, the degree varying with composition, amount of cold work, and heat treatment. Figures for magnetic induction under a field of 100 gauss and approximate transformation temperatures are given in Table II.

TABLE II.—MAGNETIC PROPERTIES.

Material.	Magnetic Induction, Gauss.	Transformation temperatures, °C.
"Monel"	1,000–1,500.	90–95.
"Monel" (cast silicon)	Non-magnetic.	Below –40.
"K Monel"	Non-magnetic.	Below –79.

*Optical Properties.*—Values for the optical reflectivity of rolled "Monel," as determined by Coblentz, are given in Table III.

*Elasticity.*—Young's modulus of elasticity for "Monel" is 26,000,000 lb. per sq. in. in tension, and 9,500,000 lb. per sq. in. in torsion.

TABLE III.—OPTICAL REFLECTIVITY OF ROLLED "Monel."

Wave-length of light in microns ( $\mu=0.011$ mm.)	Reflectivity, %.	Wave-length of light in microns ( $\mu=0.001$ mm.)	Reflectivity, %.
0.45	56.5	1.05	73.0
0.50	57.8	1.10	73.6
0.55	59.0	1.20	74.8
0.60	60.2	1.40	77.0
0.65	61.8	1.50	78.2
0.70	63.7	1.75	81.2
0.75	65.6	2.00	83.8
0.80*	67.2	2.50	87.0
0.90	70.0	3.00	88.7
0.95	71.1	3.50	89.5
1.00	72.3	4.00	91.0

\* Infra-red, where wave-length = 0.80 $\mu$  and over.

MECHANICAL PROPERTIES.

The mechanical properties of "Monel" in the hot-rolled condition approximate to those of mild steel, but the general level is raised by cold work, as may be seen from Table IV.

"K Monel," which is responsive to thermal treatment, is produced by the addition of aluminium to normal "Monel." As the thermal hardening temperature is below that at which the effects of cold work are removed, it is possible to superimpose the thermal hardening on material which has been already hardened by cold work and, in this way, to develop the maximum strength and hardness characteristics.

Typical mechanical properties, at room temperature, for the conditions in which "K Monel" is principally employed, are given in Table V.

Heat-treatment of "K Monel."—"K Monel" is softened by heating to 950–1,000°c. and quenching in water or oil. Certain thin strip sections need not be quenched, but may be cooled in air rapidly enough to retain the material in a softened condition. Heavy sections must be quenched.

Hardening of "K Monel."—"K Monel" is

TABLE IV.—RANGE OF MECHANICAL PROPERTIES OF "Monel."

Form.	Condition.	Ultimate strength, tons per sq. in.	Yield point, tons per sq. in.	Elongation on 4 $\sqrt{}$ (area), %.	Izod impact value, ft. lb.	Brinell range.
Rounds, squares, rectangles, hexagons.	Cold-rolled or drawn.	40–45	35–40	19	115–75	190–210
	Do., annealed.	30–35	14–17	35	120–90	110–120
	Hot-rolled.	34–38	15–18	35	120–100	120–140
Plate.	Hot-rolled.	34–38	15–18	35	120–100	120–140
Sheet and strip.	Cold-rolled.	45–50	40–45	15	—	200–220
	Do., annealed.	30–33	14–16	30	—	100–110
Wire.	Cold-drawn.	55–60	—	2	—	—
	Do., annealed.	29–33	14–16	35	—	—
Tubing.	Cold-drawn.	40–47	27–33	10	—	—
	Do., annealed.	29–38	11–15	20	—	—
Castings : Normal composition. Containing 3.75% of silicon.	As cast.	23–33	11–15	16–40	50–80	100–140
	As cast.	40–45	40–45	Nil	0–4	230–260*

\* Brinell hardness numbers up to 390 can be obtained with increased silicon and iron content.

TABLE V.—MECHANICAL PROPERTIES OF "K Monel."

Form.	Condition.	Ultimate strength, tons per sq. in.	Yield point, tons per sq. in.	Elongation on 4 $\sqrt{}$ (area), %.	Izod impact value, ft. lb.	Brinell range.
Rod.	Hot-rolled.	39	19	35	90	130–160
Rod.	Hot-rolled and thermally hardened.	60	43	30	50	250–280
Rod, wire, tube, strip.	Cold-worked, not thermally hardened.	—	—	—	—	200–220
Rod, wire, tube, strip.	Cold-worked and thermally hardened.	72	60	15	30	300–320
Rod, wire, tube, strip.	Cold-worked, softened, and thermally hardened.	58	40	30	30	240–270



hardened by heating to, and holding at, a predetermined temperature for a period of 1-12 hours. The temperature and the time vary with the size and previous history of the part to be treated. Figures for cold-worked "*K Monel*" are given in Table VI.

TABLE VI.—HEAT TREATMENT PROCEDURE FOR COLD-WORKED "*K Monel*."

Initial Brinell hardness.	Treatment.	Approximate final Brinell hardness.
180-230	2 hours 540-580°C., furnace cooled.	280-320
230-270	2 hours 520-560°C., furnace cooled.	320-350
270-320	8 hours 510-540°C., furnace cooled.	350-380

Slow cooling from the hardening temperature is necessary to develop maximum hardness, and should be carried out in the furnace. The rate of cooling down to 350°C. should not exceed 30° per hour.

Tensile Strengths at Elevated Temperatures.—"*Monel*" retains a high proportion of strength at temperatures up to approximately 400°C., after which there is a sharp fall. Results of tests at elevated temperatures are given in Table VII.

TABLE VII.—TENSILE TESTS OF "*Monel*" AT ELEVATED TEMPERATURES.

Temperature, °C.	Ultimate strength, tons per sq. in.	Yield point, tons per sq. in.	Elongation, %.
15	37.8	14.7	45.8
200	35.0	11.5	44.8
425	30.8	11.3	51.0
650	14.3	8.2	32.8
825	6.5	3.7	49.0

Fatigue Properties.—"*Monel*" has better fatigue properties in the "cold-worked and stress-relief annealed" condition than in the "hot-rolled" or "soft-annealed" condition.

Results of fatigue tests carried out in a rotating cantilever machine are given in Table VIII.

TABLE VIII.—FATIGUE PROPERTIES.

Material.	Condition.	Specimens remained unbroken after 10,000,000 cycles, at the stresses indicated.
" <i>Monel</i> ."	Annealed.	Plus and minus 16.5 tons per sq. in.
	Hard-drawn, stress-relief annealed.	Plus and minus 22.0 tons per sq. in.
" <i>K Monel</i> ."	Hot-rolled and thermally hardened.	Plus and minus 20.0 tons per sq. in.
	Cold-drawn and thermally hardened.	Plus and minus 22.0 tons per sq. in.

"*Monel*" has good resistance to fatigue stresses in the presence of corrosive agents. The corrosion fatigue figures in Table IX, which represent the stresses required to cause failure of specimens rotated in brackish sea-water at 1,450 r.p.m. for 10,000,000 cycles, were obtained experimentally.

TABLE IX.—CORROSION FATIGUE PROPERTIES OF "*Monel*."

Tensile strength, tons per sq. in.	Fatigue limits, ± tons per sq. in.	Corrosion fatigue limits, ± tons per sq. in.
57.6	22.0	14.5

Spring Properties.—For very light-duty springs, such as garter springs on carbon gland packings, "*Monel*" has given continuous reliable service for up to six years with superheated steam at 370°C. For heavier-duty springs, "*Monel*" should not generally be used at temperatures above 200°C.

Springs can be formed direct from hard-drawn, "spring-quality" wire. "*K Monel*" is advantageous only for springs of large size or of special types, where the ability to harden by thermal treatment after forming is an advantage. "*K Monel*" springs are serviceable in superheated steam up to about the same temperature limit as "*Monel*."

The tensile strength of hard-drawn "spring-quality" wire ( $\frac{1}{8}$  in. diameter) in "*Monel*" is above 58 tons per sq. in. Heavier wires have slightly lower tensile strengths.

Springs made from "*Monel*," after forming, should be subjected to a stress-relief anneal for 30-60 minutes at a temperature of 300°C. This gives added resiliency by improving the limit of proportionality.

Low Temperature Values.—The proof stress (or yield point), the tensile strength, and the Brinell hardness of "*Monel*" all increase as the temperature is lowered. The proof stress at -260°C. is twice that at room temperature, and the tensile strength is 65% higher. There is no loss in ductility as the temperature is decreased, the elongation at -260°C. being the same as that at room temperature and at intermediate temperatures. The modulus of elasticity tends to increase slightly as the temperature is lowered. Fatigue stress, which can be supported for a total fatigue life of 40 million cycles, is 16 tons per sq. in. at 20°C. and 17 tons per sq. in. at -40°C. Impact properties are unaffected by decrease in temperature. Welds which gave 78 ft.-lb. at room temperature gave 73 ft.-lb. at -190°C. The coefficient of thermal expansion of annealed wrought material increases slightly with decrease in temperature, and the metal becomes more magnetic.

#### RESISTANCE TO CORROSION.

"*Monel*" is highly resistant to many corrosive agents, owing primarily to its high nickel content. Variations in composition, surface finish, and physical condition have little effect on corrosion resistance.

The metal is not appreciably affected by atmospheric conditions, although it tarnishes fairly quickly, and in a city atmosphere slowly develops a green patina. It is resistant to corrosion by water, including brines, and practically immune from attack by all alkaline materials.

"Monel" is not affected appreciably by acetylene; ethyl and methyl alcohol; dry (gaseous and liquid) ammonia; ammonium chloride and sulphide; fused caustic alkalis or carbonates or their aqueous solutions; carbon dioxide and tetrachloride; petroleum and mineral oils generally; phenol and cresylic acids; dye liquors; formaldehyde; most fruit juices; pure gelatin; glycerin; hydrocyanic, hydrofluoric, and hydrofluosilicic acids; linseed oil; nitrocellulose and nitroglycerin; most vegetable oils; oxygen; perchlorethylene; potassium iodide and nitrate; radium and radium-barium concentrates; synthetic resins; latex; sodium bicarbonate, silicate, sulphate, and sulphide; starch; stearic and tannic acids; viscose; zinc chloride and sulphate.

"Monel" offers fair resistance to cold acetic acid at concentrations up to 20%. Hot acetic acid is corrosive, even in low concentrations. Aqueous chlorine and hypochlorite solutions are highly corrosive, except at very low concentrations. With the exception of mercury, low melting-point metals attack "Monel" more or less rapidly. Sulphurous, nitric, and chromic acids attack "Monel" severely. "Monel" resists attack by air-free solutions of hydrochloric acid in concentrations under 20% at atmospheric temperature, and in concentrations under 2% at higher temperatures. It resists attack by sulphuric acid, if air or other oxidising media are absent, up to about 80% concentration. Air-saturated acid of lower concentration is usually corrosive. Care must also be taken when specifying "Monel" for use with bleach liquors, citric acid, dyestuffs, hydrogen sulphide, mercuric chloride, nickel sulphate, nitrous acid, oxalic acid, phosphoric acid, tartaric acid, potassium permanganate, salt, copper slimes, soap, sodium hydroxide, sulphur chloride, sulphur dioxide, tin tetrachloride, and vinegar.

A. E. H.

MONITE (v. Vol. III, 294a).

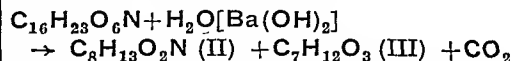
MONKEY NUTS, *pea-nuts* (v. Vol. I, 454c; VI, 138a).

MONOBEL (v. Vol. IV, 553c).

MONOCROTALINE. Greshoff for the first time mentioned the presence of an alkaloid in *Crotalaria retusa* and *C. striata* without giving any details; from *C. spectabilis* Roth the base monocrotaline was isolated by Neal, Rusoff and Ahmann (J. Amer. Chem. Soc. 1935, 57, 2560, with earlier references).

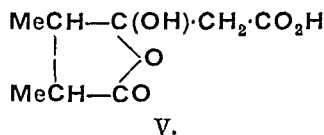
Monocrotaline (I),  $C_{16}H_{23}O_6N$  crystallises in white prisms from ethanol, m.p. 197–198° [ $\alpha_D^{26}$  –54.7° and contains no —OMe or >NMe groups. The hydrochloride, white prisms, has m.p. 184° (decomp.) and the methiodide, white prisms, m.p. 205° (decomp.). For extraction of the base, cf. Adams and Rogers (*ibid.* 1939, 61, 2815). The yield is 3.2% from seeds of *C. spectabilis* or 1.89% from seeds of *C. retusa*.

The formula  $C_{16}H_{23}O_6N$  resembles closely those of the Senecio, Heliotropium, and Trichodesma alkaloids (cf. SENECIO, ALKALOIDS OF). Hydrolysis of monocrotaline confirmed this supposition, for alkaline cleavage yielded basic retronecine (II), obtained before by hydrolysis of several Senecio alkaloids, and monocrotic acid (III) according to the following scheme:



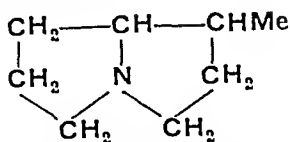
On hydrogenation monocrotaline was split into retronecanol (IV) and monocrotalic acid (V) (cf. Menshikov, Ber. 1935, 68 [B], 1051; Barger *et al.*, J.C.S. 1935, 11). The two reactions together indicate that the alkaloid is an ester of retronecine, in which one hydroxyl group of the base is covered by monocrotalic acid.

*Acidic Scission Products.*—If monocrotalic acid (V), white plates from acetone and light petroleum, m.p. 181–182°, [ $\alpha_D^{28}$  –5.33° is heated with alkali, carbon dioxide is lost (*see above*) and monocrotic acid (III), an optically inactive oil, b.p. 145–146°/18 mm. is obtained. Adams and Long (J. Amer. Chem. Soc. 1940, 62, 2289) identified (III) as dimethylævulinic acid,  $CH_3 \cdot CO \cdot CHMe \cdot CHMe \cdot CO_2H$  (m.p. of the methyl ester of the dinitrophenylhydrazones 107–109° and 121–122°, cf. Adams, Rogers, and Sprules, *ibid.* 1939, 61, 2819). The constitution of (V) is not yet established, although several alternative formulæ have been proposed (Adams and Long, *l.c.*; Adams, Rogers, and Long, *ibid.* 1939, 61, 2822) of which the following seems to be the most probable:

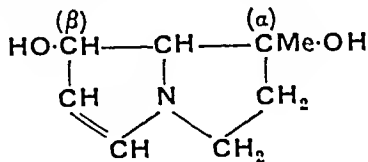


*Basic Scission Products.*—Retronecine (II) crystallises from acetone in irregular prisms, m.p. 121°, [ $\alpha_D^{28}$  +49.3°; the hydrochloride, m.p. 161–162°, forms white prisms; the picrate of the diacetyl derivative has m.p. 146°. Retronecanol (IV) forms white crystals, m.p. 95–96°, b.p. 140°/30 mm.; the hydrochloride has m.p. 210° (decomp.), and the methiodide forms white plates, m.p. 193°. Retronecine contains two hydroxyls and one double bond, whilst retronecanol is saturated and contains one hydroxyl group. The two bases are identical with those obtained by Manske (Canad. J. Res. 1931, 5, 651) and Barger and co-workers (*see above*) by similar treatment of the alkaloid retrorsine (from *Senecio retrorsus*); they are isomeric and probably stereoisomeric with the analogous basic substances from the alkaloid heliotrine (Menshikov, Ber. 1933, 66 [B], 875 and later). Many other alkaloids from several genera of plants fall into the same family in that hydrolysis and hydrogenolysis give bases identical with those resulting from retrorsine or heliotrine (cf. J. Amer. Chem. Soc. 1939, 61, 2817). Heliotridane, the parent base of the alkaloid heliotrine was shown by Menshikov and other Russian authors to be

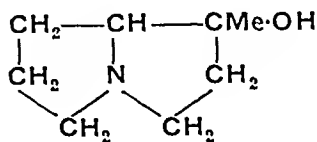
1-methylpyrrolizidine (*cf.* Adams and Rogers, *ibid.* 1941, 63, 228):



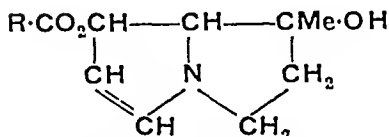
On these grounds Adams and Rogers proposed the following constitutions for (II), (IV), and (I):



II.



IV.



( $\text{R} \cdot \text{CO}_2$  represents a monocarotalic acid residue.)

I.

In (II) the two hydroxyl-groups differ in their behaviour; the  $\alpha$ -hydroxyl is tertiary and difficult to esterify, whilst the  $\beta$ -hydroxyl is very labile and prone to removal by hydrogenation (hydrogenolysis). (For further details see Adams and Rogers, *ibid.* 1941, 63, 537).

Schl.

**MONOGERMANE** (*v.* Vol. V, 521d).

**MONOLAYERS** (*v.* SURFACE FILMS).

**MONOTROPIN** (*v.* Vol. V, 503c).

**MONOTROPITIN** (*v.* Vol. VI, 92a).

**MONTAN WAX.** *Bitumen wax.* During the last fifty years, the extensive brown-coal (lignite) deposits of the Rheinland, Saxony, and Thuringia have been the site of a relatively new industry—the extraction of montan wax (von Boyen, *Chem.-Ztg.* 1903, 27, 651). For this purpose the lignite is extracted with (*e.g.*) a mixture of benzene and alcohol (G.P. 305349 523095) preferably under pressure. The evaporated extract, forming hard, brittle, dark-brown lustrous masses, is crude montan wax. It is soluble in hot light petroleum, which on cooling deposits the wax fraction while about 25% (varies greatly) of resin remains dissolved, as in the technical separation (*cf.* G.P. 523531).

*Refining.*—A yellowish-white refined wax is obtained from the crude by vacuum distillation with superheated steam (G.P. 101373). The hard black residue in the still is *montan pitch* used for moulding electrical insulators. There are numerous processes of chemical bleaching with acids or with acid chromate solutions (G.P. 493953, 503617, 523201; F.P. 829021). The acids and alcohols may be prepared from

montan wax, separately bleached, and the products esterified together (U.S.P. 1985871).

*Composition.*—Considerable variations are recorded. A sample contained: montanic acid (free) 17%, esterified 28%, aliphatic alcohols (esterified) 25%, substances of unknown constitution 30%. Tetracosanol, ceryl alcohol, and myricyl alcohol (*v.* this Vol., p. 258d) are reported as present (Pechorr *et al.* *Ber.* 1920, 53 [B], 2147; *Z. angew. Chem.* 1921, 34, 334) but wax products are frequently mixtures (Chibnall *et al.*, *Biochem. J.* 1934, 28, 2189). The best supported formula for montanic acid is  $\text{C}_{29}\text{H}_{58}\text{O}_2$ , with m.p.  $86-86.5^\circ$  (Holdo *et al.*, *Brennstoff-Chem.* 1934, 15, 311), although Tropsch and Stadler (*ibid.* 1934, 15, 201) propose  $\text{C}_{29}\text{H}_{58}\text{O}_2$ , with m.p.  $89.3^\circ$ . In addition they found the acids  $\text{C}_{25}$ ,  $\text{C}_{27}$ ,  $\text{C}_{31}$ . The acid values of a crude, distilled and bleached wax were respectively 31, 93.0, 13.6; the corresponding saponification values were 92, 94.5, 111 (Mareusson *et al.*, *Chem. Umschau*, 1931, 38, 253; B. 1931, 1000; Eisenreich, *Chem. Rev.* 1909, 16, 211). *Montanone*,  $(\text{C}_{27}\text{H}_{55})_2\text{CO}$ , the ketone of montanic acid, is the characteristic substance contained in the unsaponifiable fraction of the wax. Its reduction gives a secondary alcohol employed in testing for montan wax (Grün and Ulbrich, *Chem. Umschau*, 1916, 23, 57; *cf.* for melting-points, Easterfield and Taylor, *J.C.S.* 1911, 99, 2302).

*Uses.*—In general, montan wax replaces part or the whole of carnauba wax in shoe, floor, leather, and furniture polishes. It is a substitute for rosin in sizing paper (U.S.P. 2030385) and serves for impregnating wood (U.S.P. 2031973), for waterproofing textiles (G.P. 307111) and as an ingredient of moulding compositions (Baerlocher, *Farben-Chem.* 1938, 9, 191, 198) and candle wax (*v.* Vol. II, 264c).

*Bibliography*—H. Abraham, "Asphalt and Allied Substances," 5th ed., New York, 1945; C. Ebel, "Fabrikation von Schuhcreme," Halle a. S., 1930; E. Erdmann and M. Doleh, "Chemie der Braunkohle," 2nd ed., Berlin, 1927; E. J. Fischer, "Wachse," Dresden, 1934; W. Fuchs, "Chemie der Kohle," Berlin, 1931; H. H. Lowry, "Chemistry of Coal Utilization," New York, 1945; E. Lüddecke, "Wachse u. Wachskörper," in Ubbelohde's "Chemie u. Technologie der Öle u. Fette," Leipzig, 1926; F. Ullmann, "Enzyklopädie der technischen Chemie," 2nd ed., Berlin, 1928 (drawings of plant, Vol. II, pp. 617, 619).

J. N. G.

"MONTANIN" (*v.* Vol. IV, 23a).

**MONTEBRASITE** (*v.* Vol. I, 303d).

**MONTMORILLONITE.** A clay mineral belonging to the montmorillonite group, which also includes beidellite, nontronite, and magnesian bentonite. X-Ray diffraction studies in combination with optical examination, dehydration, and dye-absorption tests, and chemical analyses, have recently added much to the understanding of this formerly obscure group of minerals. All its members are characterised by three-layer lattico structures, thus differing from the two-layer kaolin group of minerals. The formula for montmorillonite is expressed approximately as  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , but its composition is variable owing to the wide isomorphous substitution which is possible, including the replacement of silicon by aluminium and perhaps aluminium by magnesium.

According to Nagelschmidt (Min. Mag. 1938, 25, 140) the montmorillonite group has three end-members: montmorillonite,  $\text{Al}_2\text{Si}_4\text{O}_{11}$ , nontronite,  $\text{Fe}_2\text{Si}_4\text{O}_{11}$ , and magnesium-beidellite,  $\text{Mg}_3\text{Si}_4\text{O}_{11}$ , the formulae corresponding to the completely dehydrated end-members, free from isomorphous substitutions. Each member possesses high base-exchange capacity of the order 90 milli-equivalents per 100 g., a variable basal spacing on X-ray diagrams of specimens at different moisture-contents, and a large amount of water which is reversibly absorbed or released according to the temperature and relative humidity. With fluctuation in water content the crystal lattice expands or shrinks at right-angles to the layers of the crystal structure. Most of the exchangeable base is held between the double-layer units, which are separated by one or more layers of water each approximately 3 Å. in thickness, the water being expelled at 200°C. The structure of montmorillonite is so open that water and salt solutions can easily penetrate to the interior of the crystals.

Montmorillonite crystallises in the monoclinic system, as minute scales with a lamellar structure, and has a hardness of 1-1½. It is a principal constituent of fuller's earth, an absorptive clay widely used for filtering, clarifying, and deodorising oils, greases, and fats. The important clay-like material bentonite, which occurs in sedimentary deposits derived from water-laid volcanic ash, is mainly composed of montmorillonite, together with subordinate amounts of beidellite. One variety of bentonite swells enormously in water; the other variety does not expand but has strong absorptive properties, and when activated it forms an excellent bleaching clay and oil clarifier, which is now in great demand. The swelling type of bentonite finds increasing service in reconditioning moulding sands, for rotary oil-drilling muds, and in many industrial processes.

*References.*—G. Nagelschmidt, "The Mineralogy of Soil Colloids," Imp. Bureau Soil Science, Tech. Comm. No. 42, 1944, Harpenden, England (with bibliography); *idem*, "The Identification of Minerals in Soil Colloids," J. Agric. Sci. 1939, 29, Pt. 4; *idem*, "On the Atomic Arrangement and Variability of the Members of the Montmorillonite Group," Min. Mag. 1938, 25, 140; A. N. Winchell, "Montmorillonite," Amer. Min. 1945, 30, 510; "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, New York, 1937, Chap. VI, "Bentonite," by P. Bechtner, and Chap. VII, "Bleaching Clay," by J. W. Beil and S. R. Funsten; "Bentonite," U.S. Bur. Mines, Bull. 438, 1928 (revised by J. E. Conley as Tech. Paper 609, 1940).

D. W.

MONTROYDITE (v. Vol. VII, 562d).

MOONSTONE (v. Vol. V, 3a).

MOOR-STONE (v. Vol. III, 32c).

MORDANTS (v. Vol. IV, 129d).

MORENOSITE. A hydrated nickel sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , crystallising in the orthorhombic system as acicular, fibrous, and efflorescent growths. Colour apple-green to greenish-white;  $\rho$  2, hardness 2-2½. It is a rare water-soluble alteration product of nickel sulphide ores.

D. W.

MORGANITE (v. Vol. I, 684c, 685b).

MORIN (v. Vol. I, 497d).

**MORINDA CITRIFOLIA.** The roots of *Morinda citrifolia* (Linn.) and *Morinda tinctoria* (Roxb.), known as "Morinda Root," were at one time extensively employed in various parts of India under the general trade name of "Suranji," more especially for dyeing red, purple, and chocolate shades. These plants, the native names for which are *Aal*, *A'l*, *Ach*, or *Aich*, are met with either wild or cultivated in nearly all the provinces of India. The colouring matter is found principally in the root bark and is present in greatest quantity when the plant is three or four years old; after this time the dyeing principle gradually disappears and the matured trees contain hardly a trace of it. The thin roots are most valuable, roots thicker than half an inch being rejected as worthless.

By extracting the root with alcohol, Anderson (Annalen, 1849, 71, 216) isolated a crystalline yellow substance which he termed *morindin* and this, when strongly heated, gave a crystalline sublimate of *morindone*.

*Morindin*,  $\text{C}_{28}\text{H}_{30}\text{O}_{15}$  (Anderson, l.c.);

$\text{C}_{26}\text{H}_{28}\text{O}_{14}$

(Thorpe and Greenall, J.C.S. 1887, 51, 52; Thorpe and Smith, *ibid.* 1888, 53, 171; Perkin and Hummel, *ibid.* 1894, 65, 851);  $\text{C}_{27}\text{H}_{30}\text{O}_{15}$  (Oesterle and Tisza, Arch. Pharm. 1907, 245, 534), crystallises from aqueous alcohol in glistening yellow needles, m.p. 245°, and dissolves in alkaline solutions with a red colour. According to Oesterle and Tisza (l.c.), it forms a *monoacetyl*-derivative, citron-yellow needles, m.p. 236-237°, and a *monobenzoyl* compound, yellow needles, m.p. 186°. On the other hand, Perkin (Proc. Chem. Soc. 1908, 24, 149) obtained an *octaacetyl*-derivative, pale yellow needles, m.p. 246-248° (cf. Simonsen, J.C.S. 1918, 113, 766).

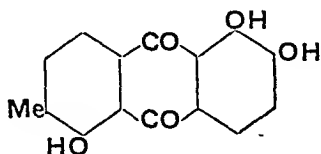
On hydrolysis with acid, morindin is converted into morindone and a sugar which is not fermented by yeast and yields an osazone, m.p. 197° (Oesterle and Tisza, l.c.), m.p. 202-203° (Perkin, l.c.).

*Morindone*,  $\text{C}_{15}\text{H}_{10}\text{O}_5$ , orange-red needles, m.p. 281-282°, may conveniently be prepared in quantity by extraction of the root with sulphurous acid according to the details given for the isolation of natural alizarin from madder (see Madder, Vol. VII, 435d). It is soluble in alkaline liquids with a blue-violet tint, somewhat bluer than the corresponding alizarin solutions, and addition of baryta water gives a cobalt-blue precipitate of the barium derivative.

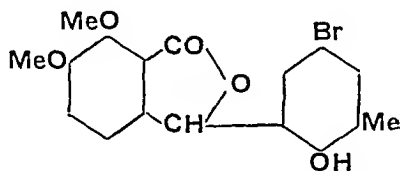
Morindone yields a *triacetyl*-derivative, citron-yellow needles, m.p. 249°, a *tribenzoyl* compound, yellow needles, m.p. 218-219°, a *monomethyl ether*, brown needles, m.p. 248°, and a *trimethyl ether*, yellow crystalline powder, m.p. 229°. On distillation with zinc dust it gives  $\beta$ -methylanthracene and is thus a trihydroxymethylanthraquinone.

This view was confirmed by Simonsen (l.c.) who found further that two of the hydroxyl groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus since treatment with methyl iodide and alkali yielded only a monomethyl ether, whilst the methyl group must be in the ortho-position to one of the hydroxyl groups, for attempts to

oxidise it to a carboxyl group by means of chromic acid proved unsuccessful. Moreover, two of the hydroxyl groups are probably in the 1:2-position since morindone is a mordant dye resembling alizarin. These and other reasons led Simonsen to conclude that morindone probably has the structure :



Jacobson and Adams (J. Amer. Chem. Soc. 1925, 47, 283) confirmed this structure by synthesis. Opianic acid and *p*-bromo-*o*-cresol, when treated with 85% sulphuric acid, give the phthalide :



and from this, by reduction, 3:4-dimethoxyphenyl-2'-hydroxy-*m*-tolylmethane-2-carboxylic acid is produced. This is converted by cold 85% sulphuric acid into 5-hydroxy-1:2-dimethoxy-6-methyl-9-anthrone and oxidised to the corresponding anthraquinone derivative. Acetylation gives 5-acetoxy-1:2-dimethoxy-6-methyl-anthraquinone which, by demethylation, is converted into 1:2:5-trihydroxy-6-methylanthraquinone, identical with natural morindone.

Morindone has also been synthesised by Bhattacharya and Simonsen (J. Indian Inst. Sci. 1927, 10 [A], 6) from 2:5-dihydroxy-6-methyl-anthraquinone which by heating with potassium hydroxide at 220–230° in the presence of sodium arsenate forms morindone.

In many respects the *Morinda citrifolia* resembles chay root and madder, for, in addition to morindin and morindone, it contains a large quantity of rubichloric acid (*v. Madder*) and certain yellow non-tinctorial derivatives of anthraquinone. Simonsen (J.C.S. 1920, 117, 561) investigated the residue remaining after extraction of morindin and isolated alizarin *α*-methyl ether and rubiadin 1-methyl ether, both of which are present in the *Morinda longiflora* (*q.v.*).

From the alcoholic extract of the *Morinda citrifolia*, Oesterle (Arch. Pharm. 1907, 245, 287), obtained a small quantity of a monomethyl ether of a trihydroxymethylanthraquinone, yellow crystals, m.p. 216°, soluble in hot alkaline solutions with a yellowish red colour. It is not, as this author suggested, identical with the emodin methyl ether present in the *Ventilago madraspatana* (Perkin, J.C.S. 1907, 91, 2074).

In addition to the above, Oesterle and Tisza (Arch. Pharm. 1908, 246, 150) isolated a monomethyl ether of a trihydroxymethylanthraquinone, m.p. 172°, and a substance, C<sub>16</sub>H<sub>10</sub>O<sub>6</sub>, m.p. 210°, which are probably identical with compounds found by Perkin and Hummel (*l.c.*)

in *Morinda umbellata*, and two dihydroxymethylanthraquinones, m.p. 244° and 276°, respectively.

**Dyeing Properties.**—In an article under the head of Morinda (Watt's "Dictionary of the Economic Products of India," 1891, Vol. V, p. 261), Dr. J. Murray gives a most complete account of the more important species and full details of the native methods of dyeing with them. These methods of dyeing vary considerably in different parts of India, but they are all similar in general principles and are practically crude processes of the Turkey-red dyeing known in Europe. Morinda root is, or was, principally used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but it is also employed for dyeing the coarse cotton cloth known as *kunda* or *khárua*, or for dyeing the silk thread which forms the border of the silk fabric known as *erendi* or *endi* cloth.

Dyeing experiments carried out by Hummel and Perkin (J.S.C.I. 1894, 13, 346) showed that by adopting certain precautions morinda root possesses a dyeing power which is greater than madder itself. To obtain satisfactory results it is necessary to neutralise or, better still, to remove the free acid which exists in considerable quantity in the roots. The dye contained in the root bark gives the best reds whereas that present in the woody part of the root is more yellow than red.

Oil-prepared calico mordanted as for Turkey-red gives a very bright orange-red or scarlet similar in shade to that given by flavopurpurin, and fast to clearing with soap and stannous chloride. Chromium mordant on similarly prepared calico gives a full rich chocolate, and iron mordant yields colours varying from dull purple to black, according to the intensity of the mordant. On wool and silk, mordanted in the usual manner, chocolate-browns are obtained with chromium, orange-reds with aluminium, bright orange with tin, and dark purple and black with iron mordants. All the colours referred to are as fast to soap as the corresponding madder colours.

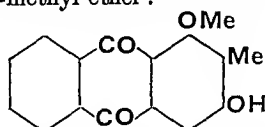
Methods of dyeing with morinda root are also described by Mell (Textile Colorist, 1928, 50, 531) and Bühler (Verh. Naturforsch. Ges. Basel, 1939, 50, 32).

E. J. C.

**MORINDA LONGIFLORA.** The *Morinda longiflora* (G. Don), known as "Ojuologbo" (woody vine) (J. Soc. Arts, 1905, 53, 1069), is a native of West Africa and considered to be one of the most valuable medicinal plants of that region. It is fully described by D. Oliver in "Flora of Tropical Africa," London, 1877, Vol. III, p. 192, where it is stated to be known under the native name of "Mbogga."

According to Barrowcliff and Tutin (J.C.S. 1907, 91, 1909) the root of the *Morinda longiflora* contains alizarin *α*-methyl ether and a rubiadin monomethyl ether, although morindin, the common constituent of the *Morinda citrifolia*, *M. tinctoria*, and *M. umbellata*, is absent. The rubiadin monomethyl ether, yellow plates, m.p. 290°, when heated with 70% sulphuric acid, gives the 1:3-dihydroxy-2-methylanthraquinone

of Schunck and Marchlewski (*ibid.* 1894, 65, 182) and has properties identical with those of rubiadin 1-methyl ether:



prepared synthetically by Jones and Robertson (*ibid.* 1930, 1699). Alizarin  $\alpha$ -methyl ether, orange-red needles, m.p. 178–179°, was first isolated by Perkin and Hummel (*ibid.* 1893, 63, 1174) from chay root and subsequently synthesised by Oesch and Perkin (Proc. Chem. Soc. 1914, 30, 213). Alizarin  $\alpha$ -methyl ether and rubiadin 1-methyl ether are also present in the *Morinda citrifolia*.

The leaves of the *Morinda longiflora* contain rubiadin 1-methyl ether and a crystalline alcohol *morindanol*,  $C_{38}H_{62}O_4$ , which melts at 278° and has  $[\alpha]_D +65.9^\circ$  in alcohol. With sodium methoxide and methyl iodide it yields methyl *morindanol*  $C_{38}H_{61}O_3$ , m.p. 116°.

"Ojuolobo" does not appear to contain an alkaloid, and extracts of the leaves and root were not found to possess any pronounced physiological action (Barrowcliff and Tutin, l.c.).

E. J. C.

#### MORINDA SPP. (v. Vol. VI, 92a).

**MORINDA UMBELLATA** or **MANG-KOUDU**. The dyeing material, variously named oungkoudou, jong-koutong, mang-koudu, etc., is the root-bark of *Morinda umbellata* (Linn.), and is met with in Eastern commerce in the form of small, reddish-brown, irregular rolls of bark, much wrinkled in appearance. In Java it is used for producing the fast reds in the native calico prints, well known under the name of "baticks."

Perkin and Hummel (J.C.S. 1894, 65, 851) examined this dyestuff and indicated its close resemblance to the *Morinda citrifolia*. In addition to morindone, they isolated the glycoside morindin (v. MORINDA CITRIFOLIA) and a considerable quantity of rubichloric acid (cf. Madder, Vol. VII, 435d), together with a small amount of non-tinctorial yellow derivatives of anthraquinone. A quantitative examination of the extract of the material with sulphurous acid (cf. Madder) gave a green precipitate which yielded crude chlororubine (4.0%), pure morindone (0.6%) and yellow substances (0.1%).

The yellow substances consisted of a mixture of at least six distinct compounds. The main constituent,  $C_{16}H_{12}O_5$ , yellow needles, m.p. 171–173°, has properties in harmony with those required by a monomethyl ether of a trihydroxy-methylanthraquinone. It forms a *diacetyl*-derivative, lemon-yellow needles, m.p. 148°.

A second compound,  $C_{15}H_{10}O_4$ , yellow needles, m.p. 269°, proved to be the methyl-purpuroxanthin (1:3-dihydroxy-6-methylanthraquinone) prepared synthetically (Marchlewski, *ibid.* 1893, 63, 1142) by the condensation of *m*-dihydroxybenzoic acid with *p*-methylbenzoic acid.

The remaining yellow substances:

(a)  $C_{16}H_{12}O_6$ ,

orange-red needles, m.p. 258°; (b)  $C_{16}H_{10}O_5$ , lemon-yellow needles, m.p. 198–199°; and (c)  $C_{16}H_{10}O_5$ , needles, m.p. 208°, were isolated in such small amount that a determination of their constitutions could not be attempted.

**Dyeing Properties.**—The colours yielded by mang-koudu are practically identical with those given by morinda root, but much fuller. In its ordinary condition mang-koudu is unsuitable for dyeing on account of deleterious acid principles present, but as in the case of A'l root, a preliminary washing or steeping in water is sufficient to remove these and to convert it into a useful red dyestuff.

E. J. C.

#### MORINDIN (v. Vol. VI, 92a).

#### MOROXITE (v. Vol. I, 449d).

**MORPHIGENINE**, 9-amino-10-hydroxy-phenanthrene hydrochloride. Narcotic (Pschorr, Ber. 1902, 35, 2729; Vahlen, *ibid.* p. 3044). Prepared by reducing phenanthraquinone monoxime with stannous chloride.

J. N. G.

#### MORPHINE v. OPIUM.

#### MORRHUIC ACID (v. Vol. III, 250c).

#### MORSE EQUATION v. MOLECULAR SPECTRA (this Vol., p. 197a).

"MORYL." "Lentin." Carbamylcholine chloride. "Doryl" (v. Vol. III, 94a); Lentin. (Veterinary use.) Parasympathetic stimulant, vasodilator (v. SYNTHETIC DRUGS).

S. E.

#### MOSAIC GOLD (v. Vol. I, 549d).

**MOSANDRITE**. Hydrated titano-silicate of cerium earths (17–26.5%), calcium, etc., occurring as reddish-brown monoclinic crystals of prismatic habit in the nepheline-syenite of the Langesundsfjord in south Norway.  $\rho$  2.93–3.03. The mineral is named after the Swedish chemist, C. G. Mosander (1797–1858), the discoverer of "didymium," lanthanum, and terbium.

L. J. S.

#### MOSELEY'S LAW (v. Vol. I, 541b).

#### MOSLENE v. TERPENES.

**MOTHER-OF-PEARL**. This is the nacreous lining of the shell of various molluscs, notably that of the large pearl-oyster *Meleagrina margaritifera* (Lam.). The nacre is secreted by the mantle of the mollusc, and consists mainly of calcium carbonate (the orthorhombic modification corresponding with the mineral aragonite) associated with organic matter (up to 12% of conchiolin). On digesting the nacre in dilute acid, all the calcareous salt may be dissolved, a coherent pellicle of connective tissue being left which retains the iridescence until disturbed by pressure. The iridescence is due to the interference of light reflected from the microscopic corrugated edges of the delicate layers of nacre. In consequence of its pleasing lustre, mother-of-pearl is largely employed for buttons, counters, card-cases, knife-handles, and a great variety of trivial ornaments. In trade three varieties of shell are recognised, viz. the white, the gold-edged, and the black-edged. Dark shells are known generally as "smoked pearl." The principal fisheries for pearl-shell are in Torres Strait, off the north-west coast of Western Australia, in the Sulu Archipelago, in the Persian



Gulf and Red Sea, and round Tahiti and some other islands of the South Pacific. In the Bay of California and the Gulf of Panama mother-of-pearl shell is obtained from the *Meleagrina californica* (Cpr.), and passes in trade as "bullock shell." The brilliant shells of the *Haliotis* and certain species of *Turbo* are also used. See W. H. Dall, Amer. Nat. 1883, 27, 579; E. W. Streeter, "Pearls and Pearl Life," London, 1886; G. F. Kunz and G. H. Stevenson, "The Book of the Pearl," New York, 1908.

L. J. S.

## MOTHPROOFING OF TEXTILES.

Insects capable of destroying keratinous materials (wool, hair, feathers) may be divided into two classes, (a) the Clothes Moths, of which *Tineola bisselliella* Hummel (the Common or Webbing Clothes Moth), *Tinea pellionella* L. (the Case-bearing Clothes Moth) and *Tricophaga tapetzella* L. (the Tapestry Moth or White-tip Clothes Moth) are the most common, and (b) the Dermestid Beetles, which are represented by *Anthrenus scrophulariæ* L. (the Common Carpet Beetle), *Attagenus piceus* Oliv. (the Black Carpet Beetle), and *Anthrenus fasciatus* Herbst. (the Furniture Carpet Beetle or "Woolly Bear"). In both types of insect, eggs are laid by the adult female from which larvæ hatch out. These feed on the keratins until eventually they pupate, and finally adult insects emerge. The time occupied by each stage varies considerably with the type of insect, temperature, and conditions of feeding, but for more details of the life history papers by Titschack (Beiträge zu einer Monographie der Kleidermotte, *Tineola bisselliella*, Z. für technische Biologie, Bd. X, Heft. 1-2, pp. 1-168, 1922); Austin and Hughes (British Museum [Natural History] Economic Pamphlet, No. 14, 1932); Benedict (Science, New Series, 1917, 46, 464); Herfs (Textilber. 1932, 13, 237); Clark (J. Text. Inst. 1928, 19, P295) and Back (U.S. Dept. of Agriculture, Farmers' Bulletin, No. 1346) should be consulted. Clothes moth larvæ are able to utilise all keratins as food, and hence wool, furs, hairs, as well as feathers and bristles, are attacked. Silk, cotton, and rayon are not eaten, although these fibres may be used to build pupa cases and are consequently occasionally damaged. "*Lanital*" (Glover, Nature, 1938, 141, 1057) and "*Nylon*" are not attacked by clothes moths. It has been shown by Burgess and Poole (J. Text. Inst. 1931, 22, T141) that keratins differ in their susceptibility to attack, the coarser fibres such as horse hair being less vulnerable than the finer ones. Similarly, the presence of certain extraneous materials, e.g., wool grease or human perspiration, on the fibres increases the possibility of destruction. In addition to keratins, Dermestid Beetles can digest proteins such as leather and the collagens, skin, cereals, and grain (Herfs, l.c.), and are also capable of damaging rayons (Herfs, Textilber. 1936, 17, 689).

The numerous methods of preserving keratinous materials from attack by insects may be classified as mechanical or chemical. Although certain of the latter undoubtedly produce the most permanent results, the actual technique adopted is dependent upon a large number of considerations, of which the limitations imposed

by the character of the material or article to be treated are the most important. For example, furniture and most garments cannot be proofed by any system which involves boiling, and hence there is still considerable value in some of the older and less efficient methods.

**Mechanical Methods.**—Although of limited application, these are extremely useful, especially for dealing with small amounts of material. Brushing and beating, accompanied if possible by exposure to direct sunlight, are often recommended for made-up garments, but are, of course, laborious and have no permanent proofing effects. To ensure satisfactory storage after beating or dry cleaning—an operation which destroys all forms of insect life—the goods should be wrapped in paper which the grubs cannot eat, or placed in air-tight containers. Any type of tough paper is suitable and the alleged superiority of newsprint is not borne out by experiment (Clark, l.c.). Trunks lined with cedar wood are frequently used for storage, although their effectiveness is due to sound construction rather than to any toxic properties of cedar wood vapour (Back and Rabak, U.S. Dept. of Agriculture, Bureau of Entomology, Bulletin 1051). Cold storage at temperatures between 18–40°F. is more satisfactory, but in general, this does not kill grubs, but merely reduces their activity (Back, U.S. Dept. of Agriculture, Farmers' Bulletin, No. 1353). To kill the insects it is necessary to submit them to two or three sudden changes in temperature. Exposure to hot sunlight or to superheated steam, hot ironing, or immersion in water (Prescott, Amer. Dyestuff Rep. 1937, 28, 90) at a temperature greater than 140°F. also kills moth larvæ but such treatments are seldom practical. A more recent method consists in exposing materials to the radiation emitted by a resistance element heated electrically so as to produce a maximum emission peak between 8,000 and 10,000 Å. (B.P. 486754).

**Chemical Methods.**—Chemical compounds may be employed either as a means of providing an atmosphere which is objectionable to insects, or to render keratins poisonous or indigestible. Reagents used as fumigants must be included in the first category, although they offer no permanent protection and are mainly useful in destroying moths and larvæ which have become a serious menace. The most effective fumigant is hydrogen cyanide (Back and Cotton, U.S. Dept. of Agriculture, Farmers' Bulletin, No. 1670) which is obtained by the action of acids on sodium cyanide, by exposing calcium cyanide to the air, or from cylinders containing liquefied hydrogen cyanide, and it is recommended to use 1 lb. of either calcium or sodium cyanide per 1,000 cu. ft. of space to be fumigated. On account of the deadly nature of hydrogen cyanide, amateurs are recommended not to use it, but to substitute sulphur dioxide [Burgess (J. Soc. Dyers and Col. 1935, 51, 85) advocates 3–4 lb. liquid sulphur dioxide per 1,000 cu. ft.], carbon disulphide (3.5–5.25 pints per 1,000 cu. ft.), or carbon tetrachloride and other halogenated hydrocarbons [14 lb. per 1,000 cu. ft. (Cotton and Roark, J. Econ. Entomol. 1927, 20, 636)]. Other less volatile compounds which

have a similar action are popularly employed in preserving keratins from damage by insects, and include naphthalene [2-3 lb. in flake form per 10 cu. ft. of space are necessary to ensure protection (Clark, *l.c.*; Back, *l.c.* No. 1352)] and paradichlorobenzene [1 lb. per 10 cu. ft. of space (Flint and McCauley, III. Agr. Expt. Sta. Circ. 1937, 473, 3)]. Both these compounds are effective only in air-tight containers or enclosed rooms, and are mainly useful for household purposes and in small storehouses. They may also be sprayed after dissolution in white spirit, alcohol or other volatile solvent.

Non-volatile substances which are toxic to moth grubs or render keratin indigestible have been shown to be more effective than the above class, and the process of mothproofing is now considered to refer to the application of these compounds. An ideal mothproofing agent should render keratins permanently immune to attack by Clothes Moths and Dermestid Beetles, and its effect should preferably be unaffected by washing or dry cleaning. It should not modify adversely those properties of fibres which render them valuable commercially, or be excessively poisonous or objectionable to human beings. It should be non-staining, and should not affect the dyeing properties of keratin either regarding fastness or shade, or alter the colour of dyed articles. Finally, the operations involved in its application should be simple and the cost low.

Inorganic compounds of this type often contain fluorine, and considerable protection is afforded by impregnation with hydrofluoric acid or its salts (Musser, J. Kansas Entomol. Soc. 1936, 9, 116), including the more complex compounds of the general formula  $MF(HF)_n$  (B.P. 295742), where M represents a metal, although sodium silicofluoride, especially if applied along with aluminium salts is more satisfactory (Minaeff and Wright, Ind. Eng. Chem. 1929, 21, 1187). Proofing is effected either by spraying with a cold saturated solution or by immersion in a 0.5% solution (Burgess, *l.c.*). As the union between keratin and sodium silicofluoride is not particularly firm, the proof is not fast to washing (Sprinkle and Slaubaugh, Text. World, 1937, 87, 2015). It is claimed that in a process using chromium fluoride (B.P. 413445) in which the material is immersed for 20 minutes at 180°F. in a solution containing 3% of the salt on the weight of the goods, squeezed and dried at about 90°C., the chromium and fluorine are chemically fixed to the keratin. Actually the fluorine is not very firmly attached as most of it is removed by washing, but the fastness is greater than is the case when sodium fluoride or sodium silicofluoride is used (Hartley, Elsworth, and Barritt, J. Soc. Dyers and Col. 1943, 59, 266). The chromium is firmly held and may be partly responsible for the considerable fastness to washing of the mothproof effect realised by chromium fluoride. Unfortunately the keratin is coloured green, but this defect may be overcome by replacing chromium fluoride by a mixture of chromium and antimony fluorides (B.P. 454458) in the ratio of 4:1. Keratins treated in this manner are not attacked either by Clothes Moths or by Dermestid Beetles. Good fastness to washing is also claimed for the

proof obtained by the following processes: (a) A reagent prepared by the addition of triethanolamine to a slight excess of fluosilicic acid, followed by the addition of aluminium sulphate and a wetting agent, is diluted and applied to wool so that 0.1-1.0% of solids are deposited (B.P. 509676). (b) Wool material is impregnated with a solution of a fluosilicate of a polymeric nitrogen-containing compound (e.g., a methylamine-phenol-formaldehyde resin) which is insoluble in water and in 5% ammonia, but soluble in 2% acetic acid, and capable of forming a coherent film. The fabric is then heated to at least 100°C. to render the fluosilicate insoluble (U.S.P. 2163104). It has recently been shown (Hartley, Elsworth, and Barritt, *l.c.*) that if 0.2-0.3% of fluorine [determined by the method of Elsworth and Barritt (Analyst, 1943, 68, 298)] is present on cloth, it may be considered to be satisfactorily proofed. To ensure this, the amount of reagent in the proofing solution must be varied according to the pH of the liquor; for example, as the acidity of the wool increases more potassium bifluoride is required to give the necessary fluorine content to the wool. Arsenites (Sprinkle and Slaubaugh, *l.c.*) and other arsenic compounds have also been used for mothproofing, but their use is limited on account of their toxicity to human beings.

Organic compounds also have found considerable application in mothproofing. Natural extracts such as those from derris and cubé roots, the active principle of which is rotenone (Cahn *et al.*, J.S.C.I. 1934, 53, 42r; 1935, 53, 37r; 1937, 56, 91r; Tattersfield, Ann. Appl. Biol. 1923, 10, 1; 1935, 22, 578; 1936, 23, 880), have the property of bringing about a general paralysis of moth larvae, but since there is a great tendency for derris extracts to lose their activity during exposure to air, the many proprietary preparations containing these mixtures often cannot be relied upon (Burgess, *l.c.*). Pyrethrum extracts obtained from the flowers of *Chrysanthemum cinerariifolium*, and containing active principles termed pyrethrin I and pyrethrin II (Hartzell and Wilcoxon, Contr. Boyce Thompson Inst. 1932, 4, 107; 1935, 5, 115; 1936, 8, 183), are also used, but like compositions containing alkaloids (Jackson and Wassel, Ind. Eng. Chem. 1927, 19, 1117; Minaeff and Wright, *l.c.*), they cannot be classed as mothproofing reagents of the first order.

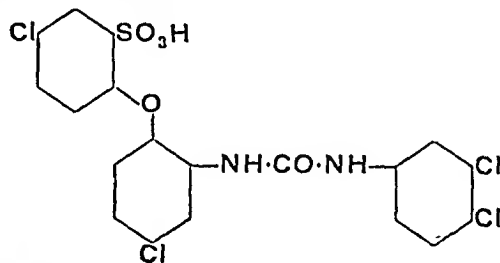
The most successful organic compounds are synthetic and are often closely related to dyes, being applied in a similar manner. It has been shown (Clark, *l.c.*) that wool dyed with Naphthol Yellow or Martius Yellow is not attacked by Clothes Moths, and therefore these reagents can be used for mothproofing when the yellow colour of the material is of no consequence. For more general use, other compounds, which may be considered to be colourless dyes, have been developed, and they are the basis of many modern mothproofing agents. Their large molecules are constituted so as to ensure firm attachment to the keratin together with toxicity to moth larvae, the latter being accomplished by the incorporation of halogen atoms. Among the more common types of compound for application in the same way as acid dyes are members



of the pentachlorodihydroxytriphenylmethane-sulphonic acid series (Herrmann, Amer. Dye-stuff, Rep. 1940, 29, 539), specific examples of which are 2:4:6:3':5'-pentachloro-3:2'-dihydroxy-4''-triphenylmethanesulphonic acid and 3:5:6:3':5'-pentachloro-2:2'-dihydroxy-2''-triphenylmethanesulphonic acid. Tetrachloro-, hexachloro-, and heptachloro-triphenylmethane-sulphonic acids also have mothproofing properties, and nitro compounds, e.g., 2:4:6:3':5'-pentachloro-3:2'-dihydroxy-4''-nitrotri-phenylmethane have a similar toxicity (B.P. 383493). Certain of the diphenylmethane derivatives are also useful (U.S.P. 1910938). For application from neutral solution, aromatic compounds of high molecular weight containing one or more pentavalent nitrogen atoms, and formed by condensing derivatives of di- or triphenylmethane with  $\beta$ -chlorotriethylamino and subsequently treating with dimethyl sulphate, may be used (B.P. 483368), whilst the phosphonium compounds, e.g., triphenyldichlorobenzylphosphonium chloride (U.S.P. 2082188), are employed in the same manner. Sulphur compounds have mothproofing properties, especially sulphonium salts of the general formula  $SR'R''R'''X$  in which  $R'$ ,  $R''$ , and  $R'''$  are aromatic residues which may be substituted or linked together in specified ways, and  $X$  is the radical of an inorganic acid, e.g., triphenylsulphonium chloride and 5-phenylthianthrenium chloride (B.P. 487804), substituted arylsulphonic esters  $R'SO_2OR''$ , where  $R'$  is a halogen-substituted benzene radical and  $R''$  an aryl radical which may be substituted with halogen or alkyl (B.P. 491434), and mercaptals, e.g., the *p*-chlorophenyl mercaptal of acetophenone (B.P. 491182). Derivatives of thiourea including phenylthiourea,  $\alpha$ -acetyl- $\beta$ -phenylthiourea, and  $\alpha$ -oleyl- $\beta$ -phenylthiourea are effective when applied from solution in organic solvents, (U.S.P. 1975408), as are derivatives of thi-anthrene (B.P. 467701), halogenated sulphides, e.g., 4:4'-dichlorodiphenylsulphide (Swiss P. 203306), and halogenated diaryl-sulphones or -sulphoxides, e.g., 4:4'-dichlorodiphenyl sulphoxide (B.P. 484448). Finally, mention should be made of an important group of mothproofing reagents (B.P. 324962), represented by the general formula  $R \cdot SO_2 \cdot NH \cdot R \cdot SO_2 \cdot NR_1R_2$ , where  $R$  is an aromatic nucleus, and  $R_1$  and  $R_2$  are hydrogen, alkyl, aryl, or aralkyl groups, the following being specific examples: *bis*-4-bromobenzenesulpho-1':3'-phenylenediamide and 1:2:5-trichlorobenzene-4-sulpho-4':6'-dichlorophenol-2'-sulpho-1':3'-phenylenediamide. Other classes of compounds which have been suggested for mothproofing include alkyl isocyanates (B.P. 512322); organic compounds containing arsenic, bismuth, tin, or antimony (U.S.P. 1766819); derivatives of phthalic acid (F.P. 713082); aryl sulphonamides (B.P. 407356); compounds containing nitrogen linked to pentavalent phosphorus, e.g., *p*-tolylxyphosphindiamide (B.P. 500386); organic compounds containing fluorine (B.P. 452579; 333583); certain aromatic hydroxy compounds, e.g., 4-methylcyclohexylphenol (B.P. 495639); derivatives of urea, e.g., sodium salt of *N,N'*-bis[2-(4-chloro-2-isopropyl-5-methylphenoxy)-

5-sulphophenyl] urea (Swiss P. 210973); compounds of the type  $R \cdot CO \cdot R'(X_n) \cdot OH$  where  $R$  is an alkyl residue with more than four carbon atoms,  $R'$  is an aryl residue and  $X$  is a halogen (B.P. 474600); non-dyeing substances containing the group  $-NR-X=Y$  where  $X$  represents nitrogen or carbon,  $Y$  represents nitrogen, carbon or a nucleus, and  $R$  represents hydrogen or an acid group, or a hydrocarbon radical, e.g., diazoaminobenzene, pyrazolone (B.P. 238287), and *o*-hydroxycarboxylic acids in which the para position is occupied by halogen or sulphur, e.g., 4-chloro-2-hydroxybenzoic acid. Further examples of the overwhelmingly large number of compounds which have been claimed to have mothproofing properties may be found in the Indexes of Mothproofing Compounds compiled by Roark (U.S. Dept. of Agriculture, Bureau of Entomology and Plant Quarantine, Division of Insecticide Investigations, 1931, 1933, 1936) and in the Annual Reports of Applied Chemistry, Fibres, Textiles, and Cellulose.

Many of the above compounds have been utilised commercially and the properties of a number of excellent mothproofing agents which have been marketed are described in detail in the technical literature (Clark, J. Text. Inst. 1936, 27, P389; J. Soc. Dyers and Col. 1943, 59, 213, and trade bulletins). The active components of some of the better known commercial products are aluminium ammonium double fluoride ("Eulan Extra"), potassium hydrogen fluoride ("Eulan W Extra"), 1-hydroxy-4-chloro-6-methyl-2-benzoic acid ("Eulan RH" and "Eulan RHF"), 2:2'-dihydroxy-3:5:3':5'-tetrachlorotriphenylmethane-2''-sulphonic acid ("Eulan N"), 3:2'-dihydroxy-2:4:6:3':5'-pentachlorotriphenylmethane-4''-sulphonic acid ("Eulan CN extra"), triphenyldichlorobenzylphosphonium oxide ("Eulan NK") (Clark, *ibid.* 1943, 59, 213), and



("Mitin FF") (Lauger, Helv. Chim. Acta, 1944, 27, 71). D.D.T. [*aa*-di-(*p*-chlorophenyl)- $\beta\beta$ -trichloroethane] has also been shown (*idem, ibid.*, p. 892) to be effective in destroying clothes-moth larvae, and may be used either as a dusting powder or dissolved in organic solvents.

A completely different principle is embodied in a method of proofing developed by Geiger, Kobayaski, and Harris (J. Res. Nat. Bur. Stand. 1942, 29, 381). The aim is to replace the  $S \cdot S \cdot$  cross linkings in the wool molecule by more stable ones and so to reduce the susceptibility of the fibre to attack, for it is believed (Linderström-Lang and Duspiwa, *Nature*, 1935, 134, 1039) that fission of the disulphide linkings is involved in the digestion of wool by clothes-moth larvae. The process consists of an initial



carboxylic acid) and gaseous decomposition products. Oxidation with permanganate gives mesotartaric acid and oxalic acid. The formation of mucic acid is frequently used to estimate galactose, galactonic acid, and galacturonic acid residues in admixture with other sugars (see C. Doré, "Methods of Cellulose Chemistry," Chapman and Hall, 1933).

It has been used (in place of tartaric acid) in baking powder, in soft drinks, in ice-cream, and in mordant dyeing. It is said to be safe for consumption by diabetics.

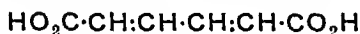
G. T. Y.

**MUCILAGES** are viscous colloidal solutions, fermentible, optically active, and precipitated by alcohol and salt solutions but not by heating (Giral, B. 1930, 211). The colloid in solution is a naturally occurring carbohydrate material (v. Gums) of complicated formula, e.g., gum arabic (Vol. I, 11d, 142d). The seed mucilages of cress, white mustard, and quince consist of a network of hydrated cellulose micelles interspersed with more heavily hydrated uronide chains. Linseed mucilage, however, is non-cellulosic (Bailey, Biochem. J. 1935, 29, 2477). Mucilages are also prepared from gum tragacanth, from starch, and from roots (Marsh Mallow, Vol. I, 263d; Salep, Vol. II, 302d). Their applications include use as adhesives, as emulsifying agents (B.P.C. 1934, 1214; Vol. IV, 285c) and in the manufacture of pills; some are also prescribed as demulcents. For the biological importance of algal mucilago, see De Wildeman, Bull. Acad. roy. Belg. 1939, [v], 25, 508.

J. N. G.

**MUCINS** (v. Vol. VI, 21c, 26a).

**MUCONIC ACID**,  $\Delta^{1,3}$ -butadiene-1:4-di-carboxylic acid,



Ingold (J.C.S. 1921, 119, 958) prepared the *trans-trans* isomer from  $\beta\beta'$ -dibromoadipic acid and by other methods, obtaining the acid as sparingly soluble crystals, m.p. 301–305° (298°, Böseken). Farmer *et al.* (*ibid.* 1923, 123, 2531; 1934, 1940) separated two isomeric methyl muconates, m.p. 156° and 75° respectively; from the latter they obtained *cis-cis*-muconic acid, m.p. 187°. Böseken *et al.* obtained this acid in 62% yield by oxidising phenol with peracetic acid (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1292), a process they regard as the simplest transition from an aromatic to an aliphatic compound. Drummond and Finar (Biochem. J. 1938, 32, 79) administered benzene to rabbits and observed the excretion of *trans-trans*-muconic acid in the urine. This biological oxidation, for which a complete proof is not claimed, has not been imitated *in vitro*. Knaggs and Lonsdale (J.C.S. 1942, 417) found that methyl *trans-trans*-muconate behaved like an aromatic compound as regards its magnetic and optical properties.

J. N. G.

**MUGUET** (v. Vol. VII, 311b).

**MULBERRY.** Trees of the genus *Morus*, the Common or Black Mulberry, *Morus nigra*, bearing dark purplish-red fruits which consist of

a number of single seeded ovaries connected together by enlarged pulpy calyces. As the fruit keeps in good condition for only a very short time after gathering, it is not of commercial importance: in the U.K. the tree is usually grown in private gardens and for ornamental purposes. *Morus rubra*, a North American species, bears dark red fruits inferior in quality to those of the Common Mulberry. The species of greatest commercial importance is the White Mulberry, *Morus alba*, which is grown extensively in the Mediterranean countries, in Asia, and in the U.S.S.R. as the leaves are the principal food of the silk-worm. The fruit is insipid and not generally eaten.

*Morus nigra*.—By reason of its relative unimportance as a commercial crop, the fruit appears to have been little studied. Its general percentage composition is as follows (König-Bömer):

Water.	Invert sugar.	Free acid (as malic).
84.7	9.2	1.9
Nitrogenous substances.	Pectin.	Ash.
0.36	2.0	0.57

The leaves are rich in calcium carbonate (2.3% of the dry substance) and the ash, which amounts to 3–4% of the dry substance, may contain up to 25% of silica. Adenine, aspartic acid, and considerable amounts of glucose have been found present in the leaves. The wood is used to some extent for inlays and veneers and it is rich in tannin.

*Morus alba*.—The nutrition of the tree and the effect on the composition of the leaf has been extensively studied from the sericultural point of view in Japan and in the U.S.S.R. (e.g., Y. Kishi, J. Agric. Chem. Soc. Japan, 1933, 9, 49, 160, 397, 412; Bull. Agric. Chem. Soc. Japan, 1935, 11, 70–77; Y. Imamura and M. Furuya, Bull. Sericult. Japan, 1932, 4, 7; K. Suda, *ibid.* 1938, 10, 89). The relations between the composition of the diet fed to the larvae and the resultant silk production have been investigated and it has been found that the accumulation of protein in the larvae is greatly dependent upon an adequate amount of carbohydrate in the leaf. It has been recommended that the yield of silk is greatest when the larvae are bred on leaves containing 3–4% of carbohydrate at the first instar period and 4–5% at the second instar. Additional carbohydrate fed with the mulberry leaves is also used to bring about an increase in the silk production.

The composition of the leaves of the White Mulberry has been given by O. M. Efimenko (Biokhim. Kul'tur. Rastenii, 1940, 7, 521, 523) who determined the main constituents as the leaves matured; the nitrogenous constituents decreased with increasing age. The figures are expressed as percentages of the dry weight:

Total nitrogen	Protein nitrogen.	Crude fat.
3.19–5.26	2.98–4.50	4.26–4.77
Crude cellulose.	Carbohydrate.	Ash.
9.39–11.19	9.24–10.40	10.21–14.46

According to A. Fujita and T. Ebihara (Biochem. Z. 1939, 300, 143), the leaves are very rich in ascorbic acid, containing 240 mg. per 100 g.

The ash of the leaves and of the wood is rich in calcium, as shown by the following values for the percentage composition of the ash :

	CaO.	Na <sub>2</sub> O.	MgO.	SiO <sub>2</sub> .	SO <sub>3</sub> .	Cl.
Leaves.	47	3.5	5-10	37.7	3.4	1.2
Wood .	54.5	13.7	—	3.4	9.8	4.7

The seeds contain a fatty oil amounting to 33% by extraction for which the following values are given:  $\rho$  0.926, sap. val. 190, iodine val. 140, Reichert-Meissl val. 0.35. The fatty acids present are chiefly liquid fatty acids (80%).

A. P.

**MULBERRY PAPER.** The bast fibres of *Broussonetia papyrifera* (Fam. Moraceae), a tree native in eastern Asia, when treated with alkalis and bleached yield a satisfactory paper pulp containing 90% of  $\alpha$ -cellulose (B. 1937, 25, 768). A fabric "tapa" is made by matting the fibres.

J. N. G.

**MULHOUSE BLUE.** *Diphenylamine Blue*. *Methyl Blue*. *Paris Blue*.<sup>\*</sup> Names formerly in use for triphenylpararosaniline hydrochloride (cf. Rowe, "Colour Index," 1924, Nos. 688, 706).

J. N. G.

**MULLITE**, aluminium silicate,



an important refractory material and a constituent of porcelain. The high-temperature diagram of the system  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  reveals only this compound; but  $\text{Al}_2\text{SiO}_5$  is of abundant occurrence in nature as the trimorphous minerals sillimanite (fibrolite), andalusite, and kyanite. At a high temperature (1,370-1,545°) these break down into a mixture of mullite and silica (as glass, cristobalite, or tridymite), and they are so employed, together with other alumino-silicates (kaolinite, topaz, dumortierite, etc.) in the manufacture of mullite. At a still higher temperature (1,810°) mullite itself breaks down to alumina (corundum) and silica. The "sillimanite" prepared by Sainte-Claire Deville and Caron in 1865 and later by other workers, and also the crystals noted in porcelain, appear in all cases to be mullite formed at a high temperature. A "sillimanite" occurring in baked fragments of aluminous slate caught up in molten igneous rock on the island of Mull has also been shown to have the composition  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and for this reason the name mullite was introduced by Bowen, Greig, and Zies in 1924. The acicular crystals of mullite are orthorhombic with a perfect pinacoidal cleavage (010), and they show no essential difference in their crystallographic, optical, and X-ray data from sillimanite. The composition of some mullite has been given as  $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , and it would seem that the material is really sillimanite containing an excess of alumina in solid solution. An analogous case is given by the artificial spinels which may range in composition from  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  to  $\text{MgO} \cdot 5\text{Al}_2\text{O}_3$ .

<sup>\*</sup> *Paris Blue* may denote Prussian Blue (v. Vol. II, 5c; III, 473b, c).

*References.*—N. L. Bowen, J. W. Greig, and E. G. Zies, J. Washington Acad. Sci. 1924, 14, 183; N. L. Bowen and J. W. Greig, J. Amer. Ceram. Soc. 1924, 7, 238; A. B. Peck, Amer. Min. 1924, 9, 123; 1925, 10, 253; J. Amer. Ceram. Soc. 1925, 8, 407; H. P. Rooksby and J. H. Partridge, Trans. Soc. Glass Technol. 1939, 23, 338.

L. J. S.

**MULTIFLORIN** (v. Vol. III, 556c).

**MULTIFUNCTIONAL ADDITIVES** (v. Vol. VII, 391d, 403b).

"**MUMETAL**" (v. Vol. VII, 458b).

**MUNDIC** (v. Vol. VII, 56a, 62a).

**MUNJEET** or **MANJEET**. The *Rubia cordifolia* Linn. was formerly extensively cultivated in India, particularly in the mountainous districts, for the sake of the colouring matters contained in its stem or roots.

By extracting the ground dyestuff with boiling alum solution, Stenhouse (Annalen, 1864, 130, 325) isolated *purpurin*, the main colouring matter, and an orange dye, termed *munjistin*, orange leaflets, m.p. 231°. The latter was subsequently shown by Schunck and Roemer (Ber. 1877, 10, 172, 790; J.C.S. 1877, 31, 666; 1878, 33, 422) to be identical with purpuroxanthin-carboxylic acid (1:3-dihydroxyanthraquinone-2-carboxylic acid), the synthesis of which was effected by Mitter and Biswas (Nature, 1930, 126, 761; 1931, 127, 166; Ber. 1932, 65 [B], 622).

Perkin and Hummel (J.C.S. 1893, 63, 1157) examined munjeet and detected the presence of a trace of purpuroxanthin in addition to the above constituents.

Munjistin is also present in madder and, together with purpurin and purpuroxanthin, in the *Rubia sikkimensis* Kurz. which is closely allied botanically to the *Rubia cordifolia* (Perkin and Hummel, l.c.).

*Dyeing Properties of Munjeet.*—The deep red aqueous extract of the ground munjeet is used generally to dye coarse cotton fabrics, or the thread which is to be woven into such fabrics, various shades of scarlet, coffee brown, or mauve. The red and chocolate shades of East India chintzes were formerly entirely obtained from munjeet. Alum appears to be generally employed as a mordant. The colours produced from munjeet are bright, but not so durable as those from madder (Watt's "Dictionary of the Economic Products of India," 1892, Vol. VI, Part I, p. 574).

E. J. C.

**MUNJISTIN** (v. Vol. V, 416b; VII, 437a).

**MUNTENITE** (v. Vol. I, 302d).

**MUREX.** *Purple of the Ancients.* *Tyrian Purple*.  $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\text{Br}_2$ . This celebrated "imperial" dye of antiquity was obtained from rock whelks found on the Mediterranean shores, chiefly *Murex brandaris* and *M. trunculus* (Vol. VI, 452c). These molluscs secrete a yellowish liquid from a small gland which on exposure to light develops a reddish-violet colour owing to the formation of an insoluble dyestuff. Silk was dyed by a kind of vat process which was very costly since 12,000 molluscs contain only 1.4 g. of dyestuff. This art of dyeing was lost about the twelfth century. Friedländer (Ber. 1909, 42, 765) showed that

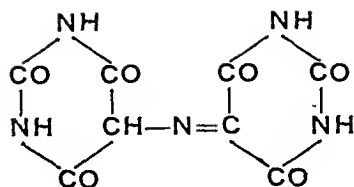
the dyestuff from *M. brandaris* was identical with 6:6'-dibromoindigotin, which, however, is inferior to the vat dyestuffs now in use and is not manufactured.

J. N. G

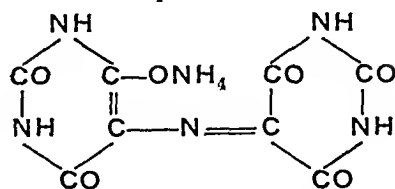
**MUREXIDE.** *Ammonium Hydrogen Purpurate*,  $C_8H_5O_6N_3 \cdot H_2O$ . Murexide is the name given by Liebig and Wöhler (Annalen, 1828, 26, 319) to the substance responsible for the deep purple colour produced when a solution of uric acid in nitric acid is evaporated and the residue treated with ammonia or an ammonium salt; this reaction constitutes the well-known test for uric acid and related purines (cf. Fischer, Ber. 1897, 30, 2236). Murexide was first obtained crystalline by Prout (Ann. Chim. Phys. 1818, [ii], 11, 48). It is the ammonium salt of a dibasic acid, *purpuric acid*, which is known only in admixture with ammonium chloride as an orange powder prepared by the action of dry hydrogen chloride on a suspension of murexide in hot anhydrous acetic acid (Möhlau and Litter, J. pr. Chem. 1906, [ii], 73, 449; acidification of salts of purpuric acid with aqueous acids causes hydrolysis with formation of alloxan, uramil, and alloxantin.

**Preparation.**—Murexide is formed (1) from uric acid as described above (Prout, *l.c.*; Liebig and Wöhler, *l.c.*), (2) by oxidation of uramil with mercuric oxide in the presence of ammonia (Beilstein, Annalen, 1858, 107, 176), or by direct condensation of uramil with alloxan (Möhlau and Litter, *l.c.*), (3) from alloxantin or alloxan, or a mixture of alloxan and ammonium diahydrate by the action of ammonia or ammonium salts under a variety of conditions (e.g., Piloty and Finckh, Annalen, 1904, 333, 22; Hartley, J.C.S. 1905, 87, 1791), (4) by the action of amino-acids on alloxan or alloxantin (Strecker, Annalen, 1862, 123, 363; Traube, Ber. 1911, 44, 3145). The yields or purity of the product obtained by the above methods render them unsuitable for preparative purposes (cf. Kuhn and Lyman, Ber. 1936, 69 [B], 1547); the method of preparation described by Davidson (J. Amer. Chem. Soc. 1936, 58, 1821) is to be preferred. A suspension of 16.1 g. finely powdered alloxantin in 1,600 c.c. glacial acetic acid is treated with 80 g. ammonium acetate with continued boiling for 1–2 minutes. The precipitated murexide is filtered, washed successively with acetic acid, alcohol, and ether, and dried; the crude product thus obtained can be purified by dissolving in water and salting out with ammonium chloride; after washing with 60% methyl alcohol and drying at 110° a 70% yield of pure murexide is obtained.

**Constitution.**—The constitution of murexide and of purpuric acid were formerly the subject of much controversy (see Piloty and Finckh, *l.c.*; Möhlau and Litter, *l.c.*; Hartley, *l.c.*; Hantzsch and Robison, Ber. 1910, 43, 92). The structure accounting best for the formation of murexide in the various ways described, and for its behaviour, is that proposed by Slimmer and Stieglitz (Amer. Chem. J. 1904, 31, 661), and this is now generally accepted (cf. Kuhn and Lyman, *l.c.*; Davidson and Epstein, J. Org. Chem. 1936, 1, 305; Winslow, J. Amer. Chem. Soc. 1939, 61, 2089):



Purpuric acid.



Murexide.

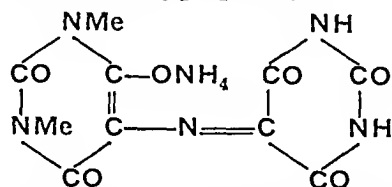
Murexide crystallises in short, four-sided, garnet-red prisms with gold-green reflex. It is sparingly soluble in cold, more readily so in hot water, insoluble in alcohol or ether. The absorption spectrum of the aqueous solution shows three bands with maxima at 520, 320, and 245 mμ., with  $\epsilon = 12.2 \times 10^3$ ,  $7.0 \times 10^3$ , and  $15.9 \times 10^3$  respectively (Kuhn and Lyman, *l.c.*).

The purity of murexide specimens can be determined by titration with sodium hydro-sulphite, which reduces murexide to a dihydro-compound with saturation of the azomethino linkago; the *leucomurexide* is a buff, micro-crystalline powder which in aqueous solution is readily re-oxidised to murexide either by atmospheric oxygen or by potassium ferricyanide (Kuhn and Lyman, *l.c.*; Davidson, *l.c.*).

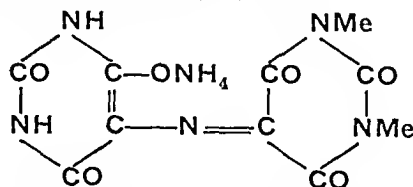
Murexide was formerly used to dye silk, wool, cotton, and leather in the presence of mercuric or zinc salts, but owing to the fugitiveness of the colours produced, its use for this purpose has been abandoned.

Metallic salts of purpuric acid can be prepared from murexide by double decomposition; they often have characteristic colours. Salts with organic bases are also known; *methylamine purpurate*, prepared by the action of methylamine on alloxan and alloxantin, forms red microscopic rhombic crystals, loses water at 110° and decomposes at 210°.

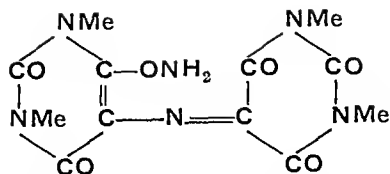
Other derivatives of purpuric acid are: *ammonium 1:3-dimethylpurpurate*,



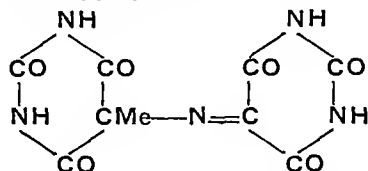
formed from 1:3-dimethyluramil and alloxan in the presence of ammonium carbonate; and *ammonium 1':3'-dimethylpurpurate*,



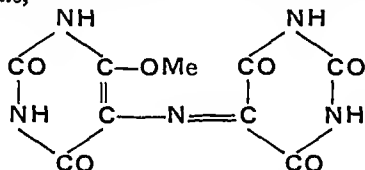
similarly obtained from uramil and 1:3-dimethyl-alloxan. *Murexoïn* (1:3:1':3' - tetramethylmurexide),



is prepared by the action of air and ammonia on malic acid (tetramethylalloxantin) (Rochleder, Jahresber. 1850, 436; Brunn, Ber. 1888, 21, 514), by treating deoxyamalic acid with bromine and afterwards with ammonia (Fischer and Ach, Ber. 1895, 28, 2477), or by electrolytic oxidation of a solution of caffeine in aqueous acetic acid (Fichter and Kern, Helv. Chim. Acta, 1926, 9, 429). It forms cinnabar-red prisms subliming without decomposition at 230°, and is sparingly soluble in water or alcohol; the solutions are deep purple-red. On warming with hydrochloric acid murexoin yields tetramethylalloxantin. *5-Methylpurpuric Acid*,

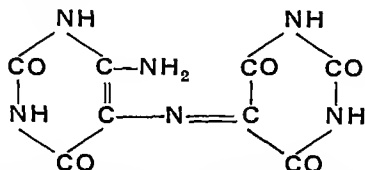


is prepared from methyl iodide and anhydrous potassium purpurate; the isomeric 4-O-methylpurpurate,

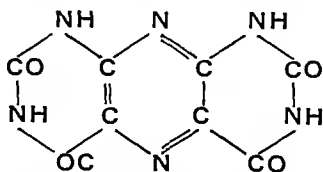


obtained from methyl iodide and silver purpurate is unstable (Slimmer and Stieglitz, *l.c.*).

#### 4-Aminopurpuric Acid,



is formed by condensing alloxan with 2:6-dioxy-4:5-diaminopyrimidine in aqueous solution. It forms brown crystals with a yellow-violet metallic surface lustre, is very hygroscopic, and cannot be recrystallised unchanged. Acidification of the solution in *N.* caustic soda yields bisalloxazine,



(Wieland, Tartter, and Purrmann, *Annalen*, 1940, 545, 209).

MURLINS (*v.* Vol. I, 199b).

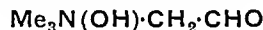
MUROMONTITE (*v.* Vol. II, 512a).

MURUMURU FAT (*v.* Vol. III, 88b, 244a).

MUSCARINE, FLY AGARIC. Mus.

carine is the toxic principle of *Amanita muscaria*, which given in traces, causes diastolic arrest of the frog's heart. The arrest is antagonised by atropine. A short historical survey on this complicated matter is given by King (*J.C.S.* 1922, 121, 1743) and by Kögl, Duisberg, and Erxleben (*Annalen*, 1931, 489, 156) as an introduction to their brilliant papers on this subject.

Muscarine (I) was first isolated in impure form by O. Schmiedeberg and R. Koppe, "*Das Muscarin*," Leipzig, 1869, by means of precipitation with potassium bismuth-iodide or potassium mercuric iodide. Harnack (*Arch. exp. Path. Pharm.* 1875, 4, 168) fractionated the impure muscarine of Schmiedeberg with aurichloride, thus removing chlorine still present. The formula  $C_5H_{13}O_2N$  was given to muscarine, which was regarded as the betaine-aldehyde or its hydrated form:



or



The non-hydrated base has been synthesised and found not to be identical with muscarine by Voet (*Bull. Soc. chim.* 1929, [iv], 45, 1016; for earlier attempts see *Berlinerblau*, Ber. 1884, 17, 1139; Fischer, *ibid.* 1893, 26, 470; and Brabant, *Chem. Zentr.* 1921, III, 124). *Cf. also* Guth, *Monatsh.* 1924, 45, 631. The betaine-aldehyde has been reported as physiologically inactive (Meyer, Ber. 1893, 26, 803) whereas Voet (*Amer. Chem. Abstr.* 1930, 24, 4843) finds that it possesses nicotine- and curare-like properties.

Synthetic or pseudo-muscarine has been obtained by Schmiedeberg and Harnack by interaction of choline with  $HNO_3$  (*Arch. exp. Path. Pharm.* 1877, 6, 101), it has a similar action to, but is not identical with natural muscarine, having a curare-like action which the natural product lacks (*cf.* Weinhausen, *Z. physiol. Chem.* 1920, 112, 13). Ewins (*Biochem. J.* 1914, 8, 209, 366) first demonstrated that the active compound obtained in the above reaction was not the hydrated betaine-aldehyde but an ester of nitrous acid and choline,

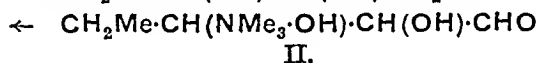
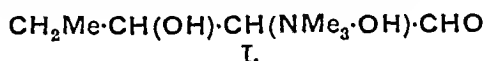


(*cf. also* Dale, *J. Pharm. exp. Ther.* 1914, 6, 147).

No further progress was made until King (*l.c.*) isolated from fly agaric in a pure state a base having in a much enhanced degree the pharmacological action characteristic of Schmiedeberg's toxic principle. (For earlier attempts, see *e.g.*, Honda, *Arch. exp. Path. Pharm.* 1911, 65, 454). King's results demonstrate that probably no one before had been working with pure muscarine, of which he only obtained 0.4 g. from 25.5 kg. of fresh fungus. King's results were extended by Kögl, Erxleben, and Duisberg (*l.c.*). They report that concentrated solutions of muscarine are easily affected by atmospheric oxygen, especially in acid solution. The preparation of pure muscarine from the crude extracts consisted in



(a) distribution between dilute ethanol and ether, (b) adsorption of foreign matter on charcoal, (c) adsorption of foreign matter by permutoite, (d) precipitation of foreign matter by mercuric chloride, (e) precipitation of muscarine with Reinecke acid and fractionation of the reineckates, and (f) preparation of the pure hydrochloride from the reineckate. The crystalline reineckate gave an analysis of the basic part corresponding to  $(C_8H_{16}O_2N)^+$ . A Hofmann degradation of the hydrochloride,  $[\alpha]_D^{20} +1.57^\circ$  (in  $H_2O$ ) afforded trimethylamine, thus confirming the quaternary character of muscarine, and an acid, m.p.  $72^\circ$ ,  $C_4H_8O_2 \cdot COOH$  which was found to be  $\alpha$ - $\beta$ -dihydroxy- $n$ -valeric acid,  $CH_2Me \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$ . Contrary to Scelba (Atti R. Accad. Lincei, 1922, [v], 31, 518) muscarine gives an Angeli-Rimini reaction and a positive Schiff's test for aldehyde, dihydroxyvaleric acid being formed by oxidation with the silver oxide used for the Hofmann degradation. Kögl concludes that the reaction takes place in the following way, (I), or less probably (II), being the constitution of muscarine:



For important work on the synthetic approach to the Muscarine problem, see Kögl and Veldstra (Annalen, 1942, 552, 1). For the toxic principle of *Amanita pantherina*, see Steidle (Chem. Zentr. 1938, II, 886). Very interesting results have been obtained by the study of *Amanita phalloides*. Phalloidine is an extremely toxic peptide,  $C_{30}H_{39}O_9N_7S$ , which is hydrolysed by sulphuric acid into cysteine, hydroxytryptophan, hydroxyproline, and alanine. As little as 0.00005 g. kills a mouse within two days. For details, see Lynen and Wieland (Annalen, 1938, 533, 93), Wieland and Witkop (*ibid.* 1940, 543, 171), and Wieland and Hallenmayer (*ibid.* 1941, 548, 1).

Schl.

**MUSCARUFIN.** The colouring matter of the fly agaric, *Amanita muscaria*, L., was first described by Griffiths (Compt. rend. 1896, 122, 1342; 1900, 130, 42) and later by Zellner (Monatsh. 1906, 27, 282).

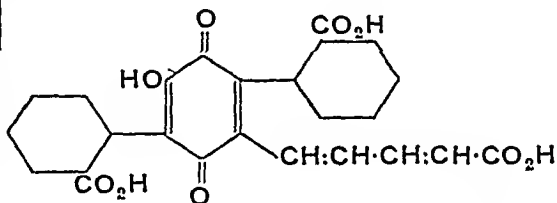
Kögl and Erxleben (Annalen, 1930, 479, 11) isolated muscarufin, which is probably present originally as a glycoside, by extracting the red skins of the fungus with alcohol at  $0^\circ$  in the dark and precipitating the colouring matter as the silver salt. This was decomposed by means of methyl-alcoholic hydrogen chloride and the resulting acid purified and finally crystallised from aqueous alcohol.

**Muscarufin**,  $C_{25}H_{16}O_9$ , orange-red needles, m.p.  $275.5^\circ$ , is optically inactive; it forms a *monoacetyl* derivative, small orange-yellow rods, m.p.  $197^\circ$ , and by reductive acetylation yields *triacyl-leucomuscarufin*, colourless needles, m.p.  $184^\circ$ , indicating that muscarufin is a quinone. The presence of three carboxyl groups is proved by electrometric titration. On distillation with

zinc dust, muscarufin is converted into terphenyl (*p*-diphenylbenzene), whilst catalytic reduction gives rise to *hexahydromuscarufin*, m.p.  $200^\circ$ , thus showing the presence of two double linkings in addition to the quinone nucleus. An alkaline solution of muscarufin (1 mol.) is oxidised by hydrogen peroxide with formation of phthalic acid (1.39 mol.), whereas similar oxidation of hexahydromuscarufin gives a mixture of phthalic and adipic acids.

The side-chain:  $—CH:CH:CH:CH \cdot CO_2H$  in muscarufin is thus indicated, and its presence is confirmed by the formation of the compound  $C_{35}H_{26}O_{15}$  by condensation of triacetyl-leucomuscarufin with maleic anhydride (*cf.* Dicks and Alder, *ibid.* 1928, 460, 102).

Accordingly, the following structure is assigned to muscarufin:



E. J. C.

**MUSCONE** (v. Vol. IV, 417a; VII, 143a).

**MUSCOVITE** (v. Vol. IV, 279d).

**MUSEUM SPECIMENS, PRESERVATION OF.** The preservation of specimens is understood to include operations related to their preparation for life in a museum and to their conservation therein. Preparation is concerned mainly with general cleaning, arresting decay and consolidating frail surfaces. Conservation is the maintaining of stability, and this subject is linked up with a study of conditions within the museum which should be such as to afford protection against all possible agencies and sources of decay, notably dust, damp, insects, and fungi.

The following important principles underlie successful preservation work:

1. No treatment is valid which detracts from the interest or value of a specimen. It is important, therefore, before commencing operations, to be clear as to wherein this lies. (For example, it may be important to preserve the exact shape of an object of corroded metal, and this may necessitate the preservation of mineralised matter which otherwise it might be wise to eliminate.)

2. The treatment which is adopted must not destroy evidence of potential value to the student. (Representative specimens of antiquities from old lake deposits or bogs which might contain membranes of microscopic pollen grains capable of affording evidence of age should be set aside for specialised examination prior to being cleaned and preserved. If this precaution is not taken such evidence as there may be will almost certainly be destroyed.)

3. Preservative processes must not be applied unnecessarily or carried to excess. (This statement is as true of the ordinary run of museum specimens as it is of oil paintings which are not slow to show the effects of so-called "over-cleaning.")



As a rule some cleaning is essential after excavation or after the effects of decay have been noticed. It is generally agreed that the sooner this is undertaken the better, and that when carried out in a sympathetic and restrained fashion the value and interest of the object in question is notably increased.

The conditions under which specimens are to remain stable (*i.e.*, conditions within the museum) will first be studied, then the principal causes of decay and their eradication. Some notes are added on maintaining stability, particularly as regards the sterilising and fumigating of collections.

#### MUSEUM CONDITIONS.

Extremes of temperature and humidity are to be avoided. High temperatures at low humidity cause adhesives to become brittle, marquetry to be damaged, bindings to be weakened, and leather to be dehydrated. High humidities, on the other hand, encourage mould growth which appears on surfaces providing nutriment, especially where there is size or glue (leather, vellum, paper).

As it has been established that fungoid growth does not take place below relative humidity (R.H.) 68%, it is desirable to set the upper limit of humidity in the museum at 65%, thus allowing a reasonable margin of safety. Any tendency for conditions to exceed this figure may be overcome by increasing ventilation and, if necessary, by heating.

There is no serious problem in this country regarding excessive dryness as figures seldom remain below 40% R.H. in storerooms for any length of time, and it is seldom worth while to introduce moisture in order to compensate for temporary losses.

In the preservation of museum specimens, temperature is seldom such an important factor as humidity. By allowing it to rise up to the limit of, say, 75°F., it can be used to control humidity, but rarely with safety beyond this. Certain classes of objects, such as carved ivories, objects repaired by wax, etc., are liable to suffer at elevated temperatures.

For the general range of antiquities, the following conditions are recommended: R.H. 40-60% (tolerance to 65%). Temperature 50-70°F. Seasonal variations within these limits must be expected, but rapid changes are to be avoided (particularly of humidity) as this causes furniture to warp, panels to crack, paint to exfoliate, etc. Steam radiators provide the worst type of heating because the rapid cooling on shutting off steam causes a correspondingly quick rise of humidity in the atmosphere. It may be noted also that damage has been caused on occasion by a picture or museum case being attached to a wall which contains panel heating. In the latter example the temperature factor is no doubt the prime cause of damage.

Considerable protection is afforded against the effects of atmospheric changes within the room by keeping specimens in boxes, vitrines or (in the case of pictures) in glazed frames. Just as conditions within the museum are less extreme than those outside in the open, so conditions within a closed case may be practically

constant (even when it is not hermetically sealed) as compared with variations within the room. Note that for the same reason dampness may persist behind bookshelves or between boxes in storage vaults, etc., and the only way to deal with this is by improving ventilation. In basement storage vaults an obvious preliminary to overcoming the effects of damp is to raise boxes at least 1½-in. above the floor on duckboarding or wooden battens, and there should be an air space of several inches next the walls. Damp air can then be cleared by the use of an electric fan or vacuum cleaner—anything to stir up the air—and it may be desirable to have ventilation holes cut at the top and at the bottom of doors. A reliable whirling psychrometer is obtainable at small cost and with such an instrument it is but the work of a few minutes to take readings of temperature and humidity and so ascertain whether conditions are satisfactory.

Paintings are very sensitive to changes in humidity. Canvases tighten in damp surroundings and the paint film may be loosened. Draughts of cold or warm air have been known to cause painted panels to crack and paint to blister. Modern practice favours the conditioning of the air of picture galleries to figures approximating to 60% R.H., 60°F., and as the conditioning process includes the removal of dust and sooty particles, it is of particular value in metropolitan areas.

The installation of conditioned air plant in a building not originally designed for it is expensive; it usually entails serious structural alteration and the results are not necessarily entirely satisfactory. It is a correspondingly simpler proposition to deal with a suite of rooms or with one special storage room. Local control within certain limits can be effected in various ways. Details have been published of a method of controlling humidity in a museum case or frame by the use of certain salt hydrates (*see* "Control of Air in Cases and Frames," by S. Cursitor, in "Technical Studies in the Field of the Fine Arts," Fogg Art Museum, Harvard University, 1936-1937, Vol. V, p. 109) and of a method of checking the tendency to rapid fluctuation of atmospheric conditions in a picture gallery (J. Macintyre, "Air Conditioning for Mantegna's Cartoons at Hampton Court Palace," *op. cit.*, 1933-1934, Vol. II, p. 171) by the (unobtrusive) storage of quantities of textiles therein.

#### MATERIAL FROM EXCAVATION.

Archæological material comes to the museum most frequently from excavation, and conditions below ground are so different from those above or from those in the museum that the change-over period is often marked by some disintegration on the part of the specimens. Metal objects which have aged gracefully for hundreds of years in the ground and acquired in the process an enamel-like protective crust of minerals known to the connoisseur as patina, may after excavation show signs of an intensification of corrosion due to the concentration of soluble salts in porous surfaces. Porous stones may be disintegrated by similar crystallisations

with the loss of important surfaces bearing ornament, perhaps, or an inscription. The cure is to remove salts, and this is usually done by washing.

Early treatment after excavation is important if serious damage is to be avoided. Treatment generally means removal of mud and soluble matter. Working details are determined by the material and the condition of the specimen. The salts are commonly a mixture with a preponderance of chlorides of the alkalis, for which the efficacy of their removal may be tested by adding silver nitrate in presence of nitric acid to a sample of the distilled-water washings; washing is normally continued until under these conditions no white precipitate is obtained.

The deterioration and treatment of the main types of antiquity will now be considered, it being understood that where there is any option, the less extreme measures are adopted. Objects from the sea or from salt desert country (e.g., Egypt and Mesopotamia) are generally in urgent need of careful preservation. The salt may or may not be visible, but if present in any quantity will sooner or later give rise to disintegration of the specimen whether it be of porous stone or metal.

**Stone and Other Porous Material.**—Salt tends to concentrate near the surface of greatest evaporation and may actually be forced out from the surface of stone in the form of a filamentous efflorescence which can be picked off with a brush. After this mechanical treatment small objects may be washed in running water whereby all the soluble matter is removed. With the larger stone objects, the primary effect of washing is to drive salts into greater depths, and washing in such cases may therefore be inadvisable. A field method of dealing with salty specimens in Egypt is to bury them in the sand which is made thoroughly wet afterwards. The heat of the sun causes evaporation at the surface of the sand to which the salts are in time transferred. The following modification of this process can be applied to the larger stones in museums. Unsized paper is boiled to pulp in distilled water and a layer of the wet pulp, half an inch thick, is applied to the stone, to which it readily adheres. Salts near the surface of the stone are dissolved and tend to make their way into the pulp. After a day or two, when the pulp is quite dry, it is removed, together with the absorbed salts. Further applications may be necessary. The process is simple, easy to apply, and in certain cases much more effective than washing.

The removal of salt is a more delicate operation where the frail surfaces bear painted ornament or inscriptions. Cuneiform tablets are an example in the latter class. As they are often made of unbaked clay, the first operation is one of baking in a sand bath for several hours at 800°C. to consolidate the clay and convert it to hard terracotta. If there should remain any doubt as to whether the incised surfaces will stand soaking in water, several coats of cellulose nitrate (2% in solvent consisting of equal volumes of amyl acetate and acetone) are applied. When the treated surface is hard and no longer sticky, washing may be carried out at the running tap and latterly, if desired, by im-

mersing in several changes of distilled water. The cellulose nitrate gives strength to the specimen but does not prevent salt being readily dissolved away, and, as chloride is always the main constituent, the progress of the washing by distilled water may be followed, as already referred to, by testing with silver nitrate. Whenever the surface of stone and like substances (pottery; earthenware) is powdery to the touch and where paint, etc., tends to flake off, washing or treatment by pulp should be preceded by surface strengthening with celluloid.

In extreme cases an Egyptian limestone may be so porous and honeycombed by crystallisations that it is advisable not to attempt to remove salt. The use of so-called stone preservatives may be dangerous, particularly those of a waxy nature. One of the most effective hardening reagents for museum work is ordinary bleached shellac dissolved in spirit, which can be run well into the stone, excess being eventually washed out of the immediate surface (which otherwise would be shiny) by using alcohol. Specimens so treated have given no further trouble over a period of twenty years in the museum, whereas others in which the action of salt has been allowed to take its course have suffered very gravely by fragments falling from the surface from time to time.

The large pottery vessels known as amphoræ, used to keep water cool by evaporation, have seldom preserved their original surfaces, these having been flaked off by salt action. Where repairs are necessary or where such a vessel has to be reconstructed from fragments, the most suitable adhesive is one that sets rather slowly, such as glue with plaster of Paris stirred into it while hot. Shellac is equally good and has the merit that it can be moulded while warm, thus allowing for modification in the position of fragments as the work proceeds.

**Metals.**—When metals corrode in the ground they become covered, as a rule, by discontinuous incrustations of mineralised corrosion products containing soluble salts. Upon excavation there may follow a period of apparent stability, but outbreaks of intensive and localised decay are to be expected as long as any chlorides remain in the incrustation. Details of treatment naturally vary to some extent with the different metals of antiquity (iron, copper and its alloys, silver, and lead) but the following processes are of general application, the object being to remove chlorides with the minimum of disturbance to the appearance of the specimen.

1. Decomposition of chlorides insoluble in water, by one of three alternatives,
  - (a) Action of special solvents.
  - (b) Reduction by electrochemical action.
  - (c) Reduction by use of electric current.
2. Washing, thereafter, until all soluble salts and especially chlorides are eliminated. This is imperative.

Mechanical picking and chipping may accompany these operations, and the work may be completed at option by polishing and lacquering. Guidance as to the choice of methods is supplied on the chart overleaf.

CHART OF METHODS EMPLOYED IN THE PRESERVATION OF METAL ANTIQUITIES.

Abbreviations: I—Imperative,  
O—Optional,  
N—Not advisable.

D—Distilled water.

V—Vinyl acetate (5%) in toluene:acetone (5:1).

O—Cellulose nitrate (2%) in acetone:amyl acetate (1:1).

Condition of Specimen.	Treatment.	Washing.	Finishing.	General Effect of Treatment.
<i>Copper and Its Alloys.</i> 1. Completely unharmed.	N.	Hot in changes of water, finally in D till free from soluble chloride.	Impregnation with V or O.	Cleaned and consolidated.
2. Newly mineralized but good metallic core remaining.	Reduce by $\text{Zn} + \text{NaOH}$ (10%), or $\text{Zn} + \text{H}_2\text{SO}_4$ (10%), or $\text{Zn} + \text{electric}$ cell or use electric current.	At running tap, finally in D as above.	As above.	Shiny metallic surface with details of ornament now visible.
3. Slightly corroded but chlorine present in quantity.	For mild treatment use cold sodium ascorbate (5%) for more drastic treatment cold citric acid (2%). Hot and more concentrated solution may be required.	As above.	Impregnation O.	Deposits on how drastic was the treatment. Cold, dilute sodium ascorbate does not destroy the patina but the patina is stripped when acids are used.
4. Having a good protective patina but with isolated spots of active decay.	Local treatment of spots by capillary tube charged with $\text{H}_2\text{SO}_4$ (conc.) used sparingly.	As above.	Lacquering N. Patina may be lightly wax polished, but only after some weeks when treatment has proved to be effective.	Disappearance of light green powdery spots (cuprous chloride), but as treatment has not been general other spots may become active in time.
5. Fallow existing with non-metallic core.	N (Uniform core can be removed, then apply 3 above).	N.	Rely on impregnation with V or O to seal residual chloride.	Core normally retains much salt but specimen treated as suggested may remain stable as long as conditions are dry.
6. Gilt bronze.	N.	Brass specimens require impregnating with 2% O prior to washing and careful cleaning.	O.	If gold attached to actual metal, the improvement in shining; but if to oxidized metal, results are uncertain.
<i>Silver</i> 1. Silver with adherent base metal corrosion (e.g., $\text{CuCO}_3$ ).	Soak for some hours in warm formic acid (50%). Ammonia (p 6-886) is rarely used as it softens horn silver and this is undesirable.	At running tap, finally in D.	With non-mercurial plate powder if desired. Lacquer V.	Green carbonate of copper removed.

2. Silver largely converted to horn silver and greatly swollen.	If metallic core remains reduce by boiling for an hour at a time with $\text{Zn} + \text{NaOH}$ (10%) or $\text{Zn}$ and formic acid (50%).	At tap. Further reduction may be necessary before D.	Old silver is very brittle especially after reduction. First it should be dried thoroughly in a steam oven, thereafter heat, <i>cautiously applied</i> and raised gradually to redness, will consolidate metal and reduce the brittleness. Such high temperatures are not possible if much horn silver is present. Lacquer V.	Shape and ornament preserved, appearance not necessarily metallic.
3. Silver objects corroded together.	Sometimes insparable without damage at least to one object. Reduction by electric current has afforded best results.	As above.		
<i>Iron.</i>				
1. Completely converted to rust.	N.	O.	By impregnation.	Consolidated.
2. Damp rust spots on metal otherwise uniformly oxidised.	Reduce by $\text{Zn} + \text{NaOH}$ (10%) or $\text{Zn} + \text{H}_2\text{SO}_4$ (10%).	At tap and with D. The final D bath should be made alkaline with $\text{NaOH}$ .	Preferably at buff with soft scratch brush. May be oiled or lacquered.	The dark clean surface shows details (damascening, chasing, engraving) well.
3. Heavy metal covered thickly with rust.	Reduce by electric current.	As above.	Some chipping may be required before buffing and impregnation.	As above.
4. Rust spots on bright armour, etc.	No chemicals; no abrasives. Soak in paraffin till rust softened.	Replace paraffin oil by sweet oil or Paraffin Moll. Alb. D.P.	Rub with soft cloth for the necessary time to polish. A film of oil may be left on armour. Steel engraved plates are usually lacquered.	Perfection of surface restored.
<i>Lead.</i>				
1. Almost completely converted to basic carbonate.	N.	N.	If worth preserving impregnate with C.	Serves little more than for record.
2. Detail masked by skin of corrosion products.	Solvent action of cold dilute acetic acid or $\text{HNO}_3$ . Neutralise, finally, with $\text{NaOH}$ .	Wash in tap water, not D.	After cleaning, fresh leaden surfaces should be exposed in an atmosphere free from chemical fumes for the time necessary to acquire a protective oxide layer (say 14 days) and specimens should not be handled during this time.	
3. Heavy specimen heavily corroded.	Reduce by $\text{Zn} + \text{NaOH}$ (10%) or by electric current.	As above.		

When special solvents are used in dilute solutions (as sodium sesquicarbonate, citric acid), it is a question of immersing the specimen for a day or so and then brushing and repeating the cycle of operations with fresh solution, persevering until positive tests are no longer obtained for soluble chloride.

The method of reduction is never selected unless a substantial core of metal remains underneath the incrustation. As an example of the method of reduction by electro-chemical action, zinc in granulated or powdered form is heaped over the corroded metal in an iron vessel and acid or alkali added, the liquor being kept at boiling-point for an hour or more. The surface of the specimen may then be brushed and the operation repeated. Similar treatment of a milder character in which the reaction takes place much more slowly may be carried out in a flat-bottomed glass vessel on the steam-bath, and this is preferable with small or delicate specimens.

In using the electric current to effect reduction, the specimen is made the cathode and is surrounded by sheet iron anodes in an electrolyte consisting of 2% caustic soda, a current of up to 5 amps. being allowed to pass for the necessary time—usually several hours and sometimes (depending on the condition of the specimen) up to about 100 hours. The current may be allowed to run up to about 10 amps. in dealing with heavily rusted iron.

#### CONSERVATION.

Protection from dust is important for the conservation of museum specimens, and improvements of comparatively recent date are the use of vacuum cleaners and dusters and of envelopes made from "cellophane" for storage purposes. Beneficial results have been especially noticeable in the case of ethnographical collections (fur; feathers; textiles), which are particularly vulnerable.

The curator has also to take measures against possible attacks by fungus and insects. While fungus (mould, mildew) can be killed off by correcting excessive humidity and by improving ventilation, as has been already described, staining may have been caused, which is not always easy to remove. The use of saponin froth is sometimes helpful in such cases or a freshly prepared 2% aqueous solution of chloramine-T; if water is undesirable good results are sometimes obtained with hydrogen peroxide in alcoholic or ethereal solution. Damp specimens may be dried and sterilised by exposure for the necessary time in a warm cupboard to the vapour of molten thymol. A 60w. lamp on a flexible lead may be placed in the cupboard, this being enough to melt the thymol crystals contained in a clock glass in contact with the lamp. When shelves of books are in question and the backs of the bindings only are affected these can sometimes be dealt with *in situ*. In such cases a 2 kw. "air-circulator" with an electric fan attachment is useful for drying and the backs of the books may then be cleaned, using a sponge moistened with a 0.5% aqueous solution of *p*-nitrophenol, which has powerful fungicidal properties. As this sub-

stance tends to impart a yellow stain the use of more concentrated solutions is undesirable.

Textile collections, fur and feathers, have to be protected against moth, and this may be done by refrigeration. It is more usual to keep specimens in envelopes which are opened and sprayed in the spring and late summer, preferably with an atomiser spray at a pressure of about 80 lb. per sq. in. Of the many types of insecticide available, preference should be given to one of the paraffin concentrates. Organic thiocyanates in paraffin have proved particularly effective without causing staining. *p*-Dichlorobenzene crystals have largely replaced camphor and naphthalene as agents for protecting the contents of exhibition cases against insect attack.

Wood beetles are dealt with by exposure (with due safeguards against fire risk) to carbon disulphide vapour. An affected panel, for example, such as a tempera or oil painting is placed in an air-tight box with several saucers of pure carbon disulphide, and the liquid renewed once in the course of a fortnight, after which the treatment is completed at option by filling the worm holes with wax. Neither paint nor varnish is affected by such treatment. The quantity of fumigant should be about one-quarter oz. per cu. ft. of air space, increasing to one ounce for thicker wooden objects, *e.g.*, furniture.

Vacuum fumigation chambers have been installed in some of the larger museums which make it possible to use ethylene oxide or hydrogen cyanide, and by this means many specimens can be dealt with at a time with the minimum of handling.

The major problems of preservation are no doubt those connected with fine art, and in this field the amateur must needs walk warily, as long years of experience are necessary for the study of various techniques employed by artists and of the effects on the original paint film of time, and of previous restorations, etc.

*Literature.*—H. J. Plendoleith, "The Preservation of Antiquities," Oxford Press, 1933; *idem*, "The Conservation of Prints, Drawings, and Manuscripts," Oxford Press, 1937; F. J. North, C. F. Davidson, and W. E. Swinton, "Geology in the Museum," Oxford Press, 1941. All aspects of the preservation of easel paintings are considered fully in "La Conservation des Peintures (Office International des Musees, Paris, 1939), and lists of qualified practitioners are kept by the Directors of Public Galleries both at home and abroad.

H. J. P.

**MUSHROOM.** A term applied to edible fungi in general, but more specifically to the Common Mushroom or Champignon, *Psaliota campestris*. Occurring naturally in fields and meadows, it is now cultured artificially on a considerable scale. The edible portion consists of the large spore-producing organ of the fungus which is itself a dense mass of filamentous threads running through the soil. Mushrooms are grown artificially by culturing a rich compost of manure or similar humus containing material with the "spawn" of mycelium. Growth is then allowed to take place under controlled conditions of temperature and humidity

in the dark (see P. A. Housman, "Licorice, Putting a Weed to Work," Twenty-sixth Stratfield Memorial Lecture, The Royal Institute of Chemistry, 1944).

Among the more common edible fungi to which the term "mushroom" has been loosely applied are related species such as *Psalliota silvatica* and other different species, e.g., *Boletus edulis*, *Boletus luteus*, *Cantharellus cibarius*, *Coprinus comatus*, *Lactarius deliciosus*, *Lepiota procera*, *Morchella esculenta* and the Truffle species (*Tuber*). Although the many edible varieties of fungi are not widely consumed in this country, they are a well-known article of food in many other regions, e.g., in the U.S.S.R. and in the East. A list of common edible and poisonous fungi is given in the Ministry of Agriculture and Fisheries publication, "Edible and Poisonous Fungi" (H.M. Stationery Office, London, 1945).

The fungi in general are of low nutritive value, the water content is high—for the common mushroom being about 90%. The protein is low (1-8%) and the carbohydrate of a non-available type. The amino-acid composition of the protein of the Common Mushroom has been studied by A. Kizel and S. Kononov (Biokhimiya, 1937, 9, 47). The carbohydrate present is trehalose and as shown by A. Ratcliffe (Biochem. J. 1937, 31, 240) it may be hydrolysed after the fungus is gathered and give rise to mannitol. Fungi are, however, relatively good sources of thiamin, riboflavin, and vitamin-D, but not of ascorbic acid. Carotene is known to occur in some species. Considerable amounts of sterols may be present and ergosterol may amount to 0.1-0.4% of the dry weight (Ratcliffe, l.c., and T. Sasaki, J. Biochem. Japan, 1939, 29, 325). The latter author also isolated from *Armillaria edodes* hydroxy- and ketostearic acids and succinic acid.

The vitamin-D present in several species of fungus has been estimated by A. Seheunert et al. (Z. physiol. Chem., 1935, 235, 91), the values being expressed in International Units per gram.

<i>Boletus edulis</i> . . . . .	0.83
<i>Cantharellus cibarius</i> . . . . .	0.83
<i>Helvella esculenta</i> . . . . .	1.25
<i>Psalliota campestris</i> (grown in dark).	0.21
" " ( " " open).	0.63

The nitrogenous constituents of mushrooms and other fungi have received considerable attention and a wide range of compounds has been found present, the bases having been chiefly studied (cf. e.g., S. Inagaki, J. Pharm. Soc. Japan, 1934, 54, 824) the presence of some of which may be connected with the particular medium on which the fungi have grown, as for example in the case of urea.

#### A. P.

**MUSK.** Musk is one of the oldest and most esteemed of the raw materials of perfumery, having great fixative value as well as a high perfume value. It is a secretion of a gland peculiar to the male deer (*v. infra*) situated in the skin of the abdomen, and appears to have some relation with the sexual organs, as it is more plentiful and more odorous when the

female is in season. The principal species of deer yielding musk is *Moschus moschiferus*, but according to the Chinese Economic Bulletin (Perfumery Record, 1933, 24, 378) *M. chrysogaler*, *M. sifanicus*, and *M. sibiricus* also yield musk in quantity worth collecting. The musk deer is found and hunted principally in Tibet, Mongolia, Nepal, Kashmir, Assam, and Surkutan, and musk is principally exported from China. From the commercial point of view, there are a number of varieties, offered under the names, Assam, Nepal, Yunnan, Tonquin, Caberdine, Shensi, and Szechuan. The locality from which the musk is exported has more connection with these names than the area of collection. The so-called *Tonquin musk* forms 80-85% of the world's supply. The musk arrives in the pods which are removed from the animal's body. The average weight is an ounce, and they should not contain more than 12-14% moisture. They are exported in boxes covered with coloured silk, containing one "catty" (about 22½ oz.), or about 22 pods. Sometimes the contents of the pod are extracted and powdered, and are then sold as "grain musk." This however obviously lends itself to gross adulteration. A pure dry musk should contain from 50-75% of matter soluble in water, and 10-15% soluble in alcohol. Moisture should be about 12-15% as determined by exposure to sulphuric acid in a desiccator, and ash 7-8%. The pod of the Tonquin musk, which is collected mainly in Tibet, is round and slightly flattened, but never pear-shaped. The so-called *Blueskin musk* is merely the ordinary Tonquin musk with the outer layers of the pod removed, leaving only the thin membranous skin which lies in contact with the secretion, and which has a steel blue colour.

Musk is usually employed in perfumery in the form of alcoholic tinctures, and so intense is its odour that one part added to 3,000 parts of an odourless powder is readily detected.

The odoriferous principle of musk is the ketone *muscone*, which is present to the extent of from 0.5 to 2% and is chemically related to *civetone* (v. Vol. VII, 143a). It is a thick colourless oil, b.p. 327-330°/752 mm., 142-143°/2 mm.,  $\rho^{15}$  0.9268. The *oxime* has m.p. 46° and the *semicarbazone* m.p. 133-134° (Walbaum, J. pr. Chem. 1906, [ii], 73, 488). For the synthesis of *dl-muscone* ( $\beta$ -methylcyclopentadecanone), see Ziegler and Weber, Annalen, 1934, 512, 164; Ruzicka and Stoll, Helv. Chim. Acta, 1934, 17, 1308.

The synthetic products known as artificial musk have no chemical relationship with natural musk, but merely have a similar odour. This, however, is much coarser than that of the natural product, and unless used sparingly the resulting perfume is coarse. There are three types of artificial musk, known as *xylene musk*, *ketone musk*, and *musk ambrette*.

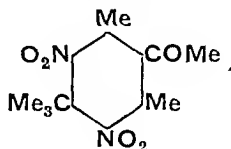
*Xylene musk* was the first known of these, and was discovered by Baur (Ber. 1891, 24, 2841); the "Musk Baur" of commerce has a dilution of acetanilide with 10% of the musk compound, described in the original patent specification as a toluene product, but the xylene homologue appears to have the better odour, and is pre-

pared by the nitration of *tert*-butyl-*m*-xylene. The nitration must be carried to the trinitro stage, as the mono- and dinitro-compounds have no marked odour of musk. The constitution of this trinitro-*tert*-butylxylene, or "xylol musk" as it is often called in commerce, is:



It has m.p. 110–113° and is soluble to the extent of about 1% in alcohol, the best solvents being benzyl benzoate and salicylate.

*Ketone musk* has a much finer odour than xylene musk, and is prepared by nitrating an acetyl derivative of *tert*-butyl-*m*-xylene; it has m.p. 136°, and has the structure



(Tschitschabin, Bull. Soc. chim. 1932, [iv], 51, 1436).

*Musk ambrette* is regarded by most perfumers as the finest of the artificial musks, it is either the methyl ether of dinitro-*tert*-butyl-*m*-cresol,  $C_6HMe(OMe)(CMe_3)(NO_2)_2$ , m.p. 85°, or a mixture of this compound with a homologue.

Artificial musks known as *aldehyde* and *cyanide musks* have been prepared, but are not commercial articles.

Artificial musks are sometimes adulterated, usually with acetanilide.

E. J. P.

**MUSTARD.** A name applied to a number of plants of the family Cruciferae cultivated all over the world. The plants are mainly grown for condimental or for the oil-bearing value of their seeds, though certain Eastern species are eaten as ordinary vegetables.

#### Cultivation.

White mustard can be grown on almost any type of land. Black mustard requires a deep well-drained fertile soil, free from acidity. In England, sowing of seed in a fine, fairly solid bed takes place in March and April. The plants ripen in August and are harvested in a similar way to ordinary cereal crops, special care being taken to ensure the dryness of the cut crop before stacking. The seeds are threshed out in the usual way.

#### Botanical Characteristics.

The most important species are as follows:

(1) *Brown (or Black) Mustard* (*Brassica nigra* Lin. Koch) is a branching annual, 3–6 ft. tall, indigenous to Europe, and is largely cultivated for its seeds. It bears four-sided pods each containing several dark reddish-brown seeds; the latter are round, about 1 mm. diameter, and finely reticulated.

(2) *White (or Yellow) Mustard* (*Sinapis alba*

Lin.) is a somewhat smaller plant, naturalised in England, and is distinguished in shape from brown mustard by its less spiky habit of growth. Its seeds are borne singly in beaked pods, and are of a light yellowish-buff colour, 2–3 mm. in diameter, and smooth to the touch.

(3) *Indian Mustard* (*Brassica juncea* Coss) is the Asiatic counterpart of *B. nigra* in Europe, and it resembles it in outward appearance. The seeds are dark reddish-brown, about 1.5 mm. in diameter, and strongly reticulated.

The above three varieties are used commercially.

(4) *Chinese Mustard* or Pak Choi (*Brassica chinensis* Lin.) and similar species (*B. pekinensis* or pe-tsai, *B. parachinensis*, etc.) are cabbage-like in appearance and are grown as vegetables in the East.

The botanical and commercial classification do not always correspond. In commercial classification the practice is adopted of naming mustard according to the region or country in which it is actually grown. Thus, the so-called Chinese mustard seed of commerce is recognised as *Brassica juncea*.

A full description of the cultivated Brassicas is given by L. H. Bailey.<sup>1</sup>

**HISTOLOGY.**—The mustard seed consists of two conduplicately folded cotyledons, enclosing an embryo, and surrounded by a spermoderm. The cotyledons consist of ordinary mesophyll tissue with aleurone and fatty granules; the spermoderm is divided into the following layers, from outside inwards:

(1) *Outer epiderm*, 50–100 $\mu$  in diameter, thin-walled mucilaginous cells.

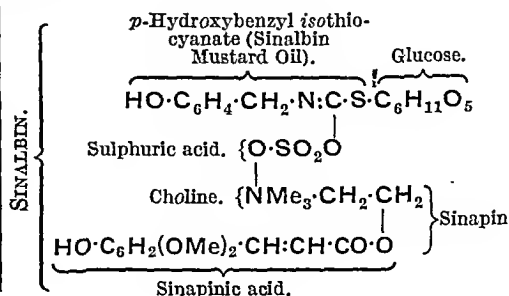
(2) *Palisade cells*, very thick-walled, about 10 $\mu$  diameter; these show well-marked polygonal dark reticulations (about 100 $\mu$ ) corresponding with the seed markings. The palisade cells are reddish-brown in the case of *B. nigra* and *B. juncea*, yellow in *S. alba*.

(3) *Pigmented layer*, thin-walled cells, about 50 $\mu$ , coloured red-brown in *B. nigra*, and *B. juncea*; in *S. alba* a layer of parenchyma takes its place.

#### Chemical Composition.

Mustards contain glucosides which hydrolyse under the action of the enzyme *myrosin* and water to yield the respective mustard oils.

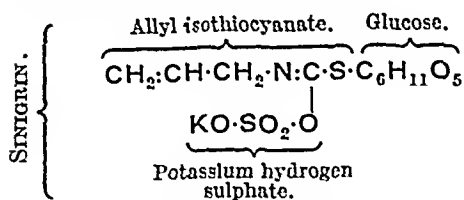
*White mustard* (*S. alba*) contains *sinalbin* (v. Vol. VI, 95d) which decomposes into its constituent components, sinalbin mustard oil, *D*-glucose, and sinapin acid sulphate, as indicated by the structural formula based on Gadamer's<sup>2</sup> results:





Sinigrin mustard oil (*p*-hydroxybenzyl isothiocyanate) is non-volatile and unstable. It possesses a pungent taste.

Brown Mustard (*B. nigra*) contains the glucoside *sinigrin* (v. Vol. VI, 96a) (*potassium myrosinate*) and hydrolyses under the action of myrosin and water into allyl isothiocyanate, *d*-glucose, and potassium hydrogen sulphate:



Allyl isothiocyanate (volatile oil of mustard) is a colourless or slightly yellow liquid, which in the crude form has b.p. 148–156°,  $\rho$  1.016–1.030; it is volatile in steam, possesses a pungent odour, and has a strong rubefacient action on the skin.

Myrosin is an enzyme which possesses the specific action of hydrolysing the mustard oil glucosides. It is present in a number of the Cruciferae family. In neutral solutions, its action is rapid, and when brown mustard flour

is mixed with water, 90% of the volatile oil (allyl isothiocyanate) is liberated in the first 8 minutes. Acids and alkalis retard or inhibit its action depending on their concentration. As is the case with other enzymes, myrosin is inactivated by boiling water. Its optimum temperature would appear to be 45–50°C.

Mustard also contains a *fixed fatty oil*, which is bland, tasteless, and nearly colourless. The general characteristics of the oils from cruciferae seeds are described by Hilditch, Riley, and Vidyarthi.<sup>3</sup> Mustard oil is used in the East for culinary purposes.

White Mustard seed contains a mucilaginous material studied by Bailey and Norris.<sup>4</sup> The mucilaginous material is in the bran, and it plays an important part in the preparation of so-called French and prepared mustards.

Mustard Flour is prepared by crushing the seeds and removing the bran by sifting. Further milling reduces the product to a fine flour. In general none of the fixed oil is removed. In some instances in the U.S.A. a portion of the oil is removed by pressing before the seed is milled, giving rise to the so-called "cake" flour.

Typical percentage analyses of mustard seed and flour are given in Table I.

TABLE I.

	Moisture.	Protein.	Fixed oil.	Allyl isothio- cyanate.	<i>p</i> -Hydroxy- benzyl iso- thiocyanate.	Ash.	Fibre.
White mustard seed .	9.3	28.4	25.6	—	2.1	4.6	10.5
Black mustard seed .	8.5	26.5	25.5	0.9	—	4.9	9.0
White mustard flour .	6.3	31.6	37.2	—	3.2	4.2	3.9
Black mustard flour .	4.3	29.8	37.0	1.4	—	5.0	3.1
Commercial blend of mustard flour . . .	4.0	34.2	35.9	0.81	1.57	4.4	—

The composition of the ash of white and black mustard seed as determined by Piesse and Stansell<sup>5</sup> is given in Table II.

TABLE II.

	K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	Cl.
White mustard seed .	22.64	0.25	11.19	12.58	1.23	41.97	8.58	1.34	0.14
Black mustard seed .	23.59	0.38	14.95	11.06	1.16	40.99	6.12	1.55	0.16

#### Standards and Adulteration of Mustard.

The U.S. Foods and Drugs Act has standards for mustard and prepared mustard which allow of no admixture with foreign starch or seeds. Many other countries prohibit any addition to mustard. In England small additions are permitted provided the product is described as a mixed article. Besides wheat flour, common additions are turmeric and cayenne pepper; all these additions may be detected microscopically. The presence of charlock (wild mustard, *B. arvensis*) in mustard is similarly detected, and also by the red colouring matter produced from the contents of the palisade cells on heating with chloral hydrate.

#### Analysis of Mustard.

The following estimations are normally carried out on samples of mustard flour:

*Moisture*.—Owing to decomposition losses, this is determined by drying *in vacuo*.

*Ash, Protein, and Fixed Oil* are determined by normal methods.

*Crude Fibre* is estimated by the usual A.O.A.C. method.<sup>6</sup>

*Sinigrin and Allyl Mustard Oil* are normally estimated by the method of the French Codex<sup>7</sup> with the modification that the initial resolution or hydrolysis to produce the pungent principles is permitted to proceed for 2 hours at 37°C.

*Sinigrin and p-hydroxybenzyl isothiocyanate* may be determined by the method of Terry and Corran.<sup>8</sup>

### Uses of Mustard.

Whole mustard seed is used as a flavouring in pickles, sauces, etc. The co-called prepared mustard of commerce in the U.S.A., and various continental mustards, consist of the whole seeds ground to a fine paste with vinegar, salt, and spices. The consistency and smoothness of the mustard, which depends on the mucilaginous material present in the outer coatings of the white seed, is determined by the fineness of the grinding process. In England, mustard flour made into a paste with water or milk is one of the recognised condiments. The mustard flour used is a blend of white and brown mustard flours and when mixed with water the pungent oils are released. Almost complete liberation of these oils is attained in 8-10 minutes after the mixing. The condimental use of mustard is largely a fact of experience and is based on the elusive factors of flavour and palatability. In the manufacture of salad cream and mayonnaise, mustard flour exerts a strong emulsifying action, enhancing the stability and increasing the initial consistency of the mayonnaise emulsion (Corran<sup>9, 10</sup>). In this connection mustard acts as a fine powder and favours the formation of an oil-in-water emulsion. Mustard flour also possesses adsorptive properties which have been made particular use of in the wine industry to remove taints and mustiness from wines.<sup>11-16</sup> Experiments have shown that both brown and white mustard have a powerful fungicidal action against the yeasts of alcoholic fermentation and compare in effect with chemical preservatives such as sulphur dioxide and benzoic acid.<sup>17</sup> Of the spices and condiments, mustard, through its essential oils, is the most powerful in its fungicidal action. Fungi of the genera *Epidermophyton* and *Trichophyton*, responsible for ring-worm infections of the hands and feet, are also inhibited or killed by mustard, while the common fungi of the air show varying degrees of resistance to its action.

### Physiological Aspects of Mustard.

Mustard is classed pharmacologically as a rubefacient and counter-irritant, these properties being due to the pungent oils which are produced on moistening the dry mustard flour with water. Of the two oils, allyl isothiocyanate (volatile oil of mustard) seems to have received attention by physiologists and more is known of its physiological action than is the case of *p*-hydroxybenzyl isothiocyanate, the oil obtained from white mustard.

Mustard mixed with water to liberate the pungent principles and then applied to the skin causes a dilation of the capillaries resulting in a flow of blood therein from the neighbouring larger vessels and from the deeper-seated organs beneath. This is manifested by a reddening of the skin at the site of treatment, and by the production of warmth and tingling sensations which may become unbearable. At the same time the capillary walls increase in permeability, with consequent exudation of fluid into the tissue spaces, eventually leading to the formation of a weal. These phenomena have been explained by Lewis<sup>18</sup> as being due to the production of a

histamine-like substance which initiates the responses described above. Similar effects are produced by heat, cold, electric currents, and various trauma.

Allyl (brown) mustard oil, being volatile, causes violent irritation to the eyes and nasal passages even at a distance, but oil of white mustard is non-volatile, and, therefore, does not have this action. Another difference in their physiological effects is that white mustard produces the skin reactions more slowly than does brown, but once initiated they persist for a longer time.

Mustard also has a reflex stimulating action upon the heart, which tends to neutralise the depression that would otherwise follow the initial stimulations. This property makes a thin suspension of mustard one of the safest emetics.

Applications of mustard are used in medical treatment chiefly for alleviation of pain. This effect results partly from the warmth produced, partly from the draining away of blood from deep-seated organs with consequent relief of pressure therein, and to some extent no doubt from the reflex nervous stimulation referred to above. In mustard therapy the normal procedure is to mix the flour with cold or tepid water in order to liberate the oil, and apply it as a poultice, plaster, or pack. Details of the therapeutic uses and modes of application of these are given in most textbooks of physiotherapy or nursing.

### REFERENCES.

- <sup>1</sup> L. H. Bailey, *Gentes Herbarum*, 1930, [v], 2, 211.
- <sup>2</sup> Gadamer, *Arch. Pharm.* 1897, 235, 83; *Ber.* 1897, 30, 2322-2334.
- <sup>3</sup> Hilditch, Riley, and Vidyarthi, *J.S.C.I.* 1927, 46, 457-462t.
- <sup>4</sup> Bailey and Norris, *Biochem. J.* 1932, 26, 1609-1623.
- <sup>5</sup> Piesse and Stansell, *Analyst*, 1880, 5, 161.
- <sup>6</sup> Association of Official Agricultural Chemists, "Methods of Analysis," 4th ed., 1935, p. 340.
- <sup>7</sup> D. Raquet, *J. Pharm. Chim.* 1920, 22, 92.
- <sup>8</sup> Terry and Corran, *Analyst*, 1939, 64, 164.
- <sup>9</sup> Corran, *Food Manufacture*, 1934, 9, 17.
- <sup>10</sup> J. W. Corran, "Technical Aspects of Emulsions," A. Harvey, London, 1935, p. 90 (Report of a Symposium held under the auspices of the Int. Soc. of Leather Trades Chemists).
- <sup>11</sup> Moreau and Vinet, *Ann. Falsif.* 1924, 17, 477.
- <sup>12</sup> Roos and Hughes, *ibid.*, p. 413.
- <sup>13</sup> Delage, *ibid.* 1923, 16, 483.
- <sup>14</sup> Ferré, *ibid.* 1925, 18, 34.
- <sup>15</sup> Grove, *Ann. Rept. Long Ashton*, 1918.
- <sup>16</sup> Lahache, *L'Ind. franc. conserve*, 1919, 5, 211.
- <sup>17</sup> Corran and Edgar, *J.S.C.I.* 1933, 52, 149t.
- <sup>18</sup> Sir Thomas Lewis, "The Blood Vessels of the Human Skin and Their Responses," London, 1927.

J. W. C.

### MUSTARD, ESSENTIAL OIL OF.

*Cf. MUSTARD*, this Vol., p. 254b). This oil is obtained from the seeds of the black mustard, *Brassica nigra* Koch (Fam. Cruciferae), after expressing the fixed oil. The pressed cake is macerated in water at 60-70° for several hours when a reaction takes place between the glucoside sinigrin (potassium myronate) and the enzyme myrosin, present in the seed, with the production of allyl isothiocyanate, the main constituent of the oil.

*Composition*.—Allyl isothiocyanate 93-98% with traces of carbon disulphide and allyl cyanide. Artificial mustard oil is obtained by

the dry distillation of potassium allyl sulphate and potassium thiocyanate, or by heating allyl bromide with an alcoholic solution of potassium thiocyanate. It is largely used in place of the natural oil of mustard.

**Properties.**—Essential oil of mustard is a colourless or slightly yellowish liquid,  $\rho$  1.018–1.024, which has highly lachrymatory and vesicant properties. It is said to prevent the souring of red wines if added in the proportion of 1 c.c. of a 1% solution to 1 litre of wine. In this proportion it is stated to affect neither the odour nor the flavour.

C. T. B.

**MUSTARD GAS** (v. Vol. III, 8d, 11b, 21d, 22a).

**MUTAROTATION** (v. Vol. VII, 70c).

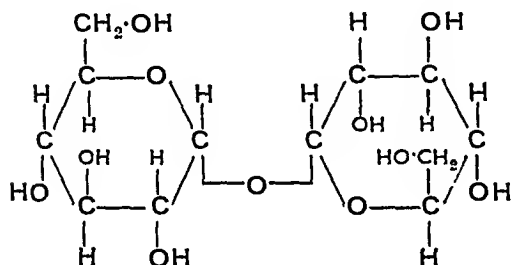
**MUTASE** (v. Vol. V, 429b).

**MYCODEXTRAN** (v. Vol. V, 57d).

**MYCOGALACTAN** (v. Vol. V, 58a).

**MYCOPHENOLIC ACID** (v. Vol. V, 53c).

**MYCOSE** is  $\alpha$ -trehalose,  $\alpha$ -diglucofuranose:



G. T. Y.

**"MYOCHRYNIN"** (v. Vol. VI, 119b). Sodium aurothiomalate. Used in treatment of tuberculosis and rheumatoid arthritis (v. SYNTHETIC DRUGS).

S. E.

**MYOCTONINE** (v. Vol. I, 123d).

**MYOGLOBIN** (v. Vol. VI, 166d).

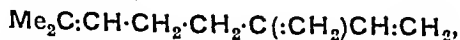
**MYOKYNINE** (v. Vol. I, 687b).

**"MYOSALVARSAN"** (v. Vol. I, 492a).

**MYOSIN.** *Paramyosinogen*. A protein of the globulin class found in striated muscle and in maize (Vol. II, 481d). For its structure, elasticity, and relation to muscular contraction, see Astbury *et al.*, Proc. Roy. Soc. 1940, B, 129, 307; Astbury, J.C.S. 1942, 337. Amino-acids amounting to 77% of its weight have been identified by Sharp (Biochem. J. 1939, 33, 679).

J. N. G.

**MYRCENE,**



b.p. 166–168°/760 mm.,  $\rho^{25}$  0.8013,  $n_D^{25}$  1.4700, occurs in the essential oils from the leaves of *Myrcia acris* and *Barosma venusta* and in a number of other essential oils (v. TERPENES).

J. L. S.

**MYRCENOL.** This alcohol,  $\text{C}_{10}\text{H}_{18}\text{O}$ , b.p. 99°/10 mm.,  $\rho^{15}$  0.9032,  $n_D^{15}$  1.4806, of unknown constitution is stated to occur in the oil from the leaves of *Barosma venusta* and in oil of hops. It is not identical with the alcohol obtained by the oxidation of myrcene with selenium dioxide which has been similarly designated (v. TERPENES).

J. L. S.

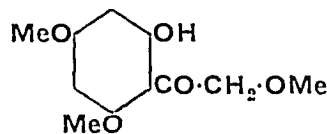
**MYRICA NAGI** Thunb., an evergreen tree belonging to the *Myricaceae* is found in the sub-tropical Himalayas from the Ravi eastwards, also in the Khasia mountains, the Malay Islands, China, and Japan. It is the box-myrtle or *Yangmæ* in China and is synonymous with *M. sapida* Wall., *M. rubra* Sieb. and Zucc., and *M. integrifolia* Roxb. The bark, occasionally used as a tanning agent, is met with under the name of *kaiphal* (Bombay) or *shibuki* (Japan).

The colouring matter, *myricetin*, and its glycoside, *myricitrin*, can be isolated from an aqueous extract of the plant, but are more readily obtained in quantity from commercial "shibuki" extract (Perkin and Hummel, J.C.S. 1896, 69, 1287; Perkin, *ibid.* 1902, 81, 204).

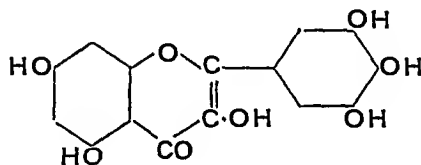
*Myricetin*,  $\text{C}_{15}\text{H}_{10}\text{O}_6$ , pale yellow needles, m.p. 357–360°, is soluble in aqueous potassium hydroxide with a green coloration which, on standing in air, becomes first blue, then violet, and eventually brown. Alcoholic lead acetate gives an orange-red precipitate and ferric chloride a brown-black coloration. With mineral acids in the presence of acetic acid it yields crystalline oxonium salts.

The following derivatives of *myricetin* have been prepared: *Hexa-acetate*, colourless needles, m.p. 214–215°; *tetrabromo-derivative*, brown-red needles, m.p. 235–240°, and its *ethyl ether*, m.p. about 146°; *3':5'-dimethyl ether*, pale yellow needles, m.p. 288–289° after darkening at about 270°; *3':4':5'-trimethyl ether*, pale yellow needles, m.p. 290–293°; *3:3':4':5'-tetramethyl ether*, pale yellow plates, m.p. 276–277.5°; *3:7:3':4':5'-pentamethyl ether*, very pale yellow needles, m.p. 138–139°; *5:7:3':4':5'-pentamethyl ether*, yellow needles, m.p. 230°; *hexamethyl ether*, colourless needles, m.p. 159–161°; *heptaethyl ether*, almost colourless needles, m.p. 149–151°.

When fused with alkali *myricetin* yields phloroglucinol and gallic acid. With boiling alcoholic potash *myricetin* hexamethyl ether gives gallic acid trimethyl ether and methoxyfisetol dimethyl ether (I); *myricetin* is, therefore, 3:5:7:3':4':5'-hexahydroxyflavono (II) (Perkin, *ibid.* 1911, 99, 1721).



I.



II.

This structure has been confirmed by synthesis (Kaff and Robinson, *ibid.* 1925, 127, 181).  $\omega$ -Methoxyphloracetophenone was heated with trimethyl gallic anhydride and sodium trimethyl gallate and the product hydrolysed; the 5:7-dihydroxy-3:3':4':5'-tetramethoxyflavone thus obtained yielded *myricetin* on demethylation.

Myricetin 3':4':5'-trimethyl ether and syringetin (myricetin 3':5'-dimethyl ether) were similarly prepared (Heap and Robinson, *ibid.* 1929, 67).

The synthesis of myricetin pentamethyl ether was effected by Sonn (Ber. 1925, 58 [B], 1103) by the condensation of 2-hydroxy-4:6-dimethoxyacetophenone and 3:4:5-trimethoxybenzaldehyde; the 2-hydroxy-4:6-dimethoxyphenyl 3:4:5-trimethoxystyryl ketone formed was converted into the flavanone, the oximinoderivative of which was transformed by sulphuric and acetic acids into myricetin 5:7:3':4':5'-pentamethyl ether (*cf.* Dean and Nierenstein, J. Amer. Chem. Soc. 1925, 47, 1676; Nierenstein, Ber. 1928, 61 [B], 361; and Hattori, Bull. Chem. Soc. Japan, 1927, 2, 171).

*Myricitrin* crystallises from water forming pale yellow, almost colourless leaflets, m.p. 199–200°, and is soluble in alkalis with a pale yellow tint. Aqueous lead acetate gives an orange-yellow precipitate and alcoholic ferric chloride a deep greenish-black coloration. On hydrolysis it yields myricetin and rhamnose.

By methylating myricitrin with diazomethane, or with dimethyl sulphate and alkali in an atmosphere of hydrogen, and hydrolysing the product, Hattori and Hayashi (Acta Phytochim. 1931, 5, 213) obtained myricetin 5:7:3':4':5'-pentamethyl ether. They conclude, therefore, that the rhamnose residue in myricitrin is in the 3-position.

In addition to myricetin, the *M. nagi* contains a trace of a glycoside of a second colouring matter which is probably quercetin.

Myricetin is also present in the leaves of *Rhus coriaria*, *cotinus*, and *metopium*, in the *Myrica gale*, in the leaves of *Pistacia lentiscus*, *Hæmatoxylon campechianum*, and *Coriaria myrtifolia* (Perkin, J.C.S. 1898, 73, 1016; 1900, 77, 426; Perkin and Allen, *ibid.* 1896, 69, 1299; Perkin and Wood, *ibid.* 1898, 73, 376), and together with *ampelopsin* (3:5:7:3':4':5'-hexahydroxyflavanone) in "Haku-tya" (*Ampelopsis meliifolia*, Kudo) (Kotake and Kubota, Annalen, 1940, 544, 253). Myricitrin has been isolated from the leaves of the hazel nut, *Corylus avellana*, and the Judas tree, *Cercis siliquastrum* (Collot and Charaux, Bull. Soc. Chim. biol. 1939, 21, 455).

The pharmacological action, particularly the diuretic action, of myricetin and related compounds has been studied by Koike (Folia Pharmacol. Japan, 1931, 12, No. 1, 89, Breviaria, 6).

Myricetin may be used to determine small amounts of antimony (Naito, J. Pharm. Soc. Japan, 1939, 59, 303).

For reduction products of myricetin and myricitrin, and absorption spectra, see Kondo (*ibid.* 1932, 52, 353), Moir (J. S. African Chem. Inst. 1927, 10, 36), and Tasaki (Acta Phytochim. 1927, 3, 1).

**Dyeing Properties.**—On mordanted woollen cloth the shades given in the Table are obtained.

The shades obtained with myricetin and myricitrin are practically identical with those given by quercetin and quercitrin, respectively. Myrica bark gives shades which are similar to the colours obtained from quercitrin bark, but are fuller. According to Hummel and Perkin

(J.S.C.I. 1895, 14, 458), some specimens of myrica bark are exceedingly rich in colouring matter.

By fusing myricetin with sodium polysulphide and sulphur, Satow (Ind. Eng. Chem. 1915, 7, 113) obtained a product which dyes cotton a

	Chromium.	Aluminium.	Tin.	Iron.
Myricetin . .	Red-brown.	Brown-orange.	Bright red-orange.	Olive-black.
Myricitrin . .	Full brown-yellow.	Full golden yellow.	Lemon-yellow.	Brown-olive.
Myrica bark .	Deep olive-yellow.	Dull yellow.	Bright red-orange.	Dark greenish olive.

deep sepia colour, though if copper sulphate, manganese sulphate, or ferrous sulphate is added to the fused mass, substances possessing a bluish or bluish-grey colour are produced. When fused with sulphur alone, myricetin gives a brown-yellow compound. A yellow dye may also be obtained by nitrating myricetin sulphonic acid.

E. J. C.

**MYRICIN**, originally the residue obtained by extracting beeswax with boiling alcohol (Brodie, Phil. Trans. 1849, 139, i, 91); its chief constituent, melissyl palmitate, m.p. 72°, is usually known as *myricin*. Melissyl alcohol (*v. infra*) from beeswax is a mixture of alcohols. In pharmacy *myricin* denotes the powdered extract of bayberry bark ("Extra Pharmacopœia," 1941, I, 375).

J. N. G.

**MYRICITRIN** (*v. supra* and Vol. VI, 92b).

**MYRICYL ALCOHOL.** *Melissyl alcohol.* *Melissic alcohol.* There has been much confusion in the literature concerning the formula of this normal primary alcohol, which has been frequently reported either as  $C_{30}H_{61}OH$  or as  $C_{31}H_{63}OH$  (*cf.* "Beilstein," Zweites Ergänzungswerk, 1941, I, 472).

Heiduschka and Gareis (J. pr. Chem. 1919, [ii], 99, 298) assigned the  $C_{30}$  formula to carnauba wax melissyl alcohol, m.p. 87.5° and the  $C_{31}$  formula to beeswax melissyl alcohol, m.p. 85.5°. Gascard and Damoy (Compt. rend. 1923, 177, 1442) confirmed the  $C_{31}$  formula last-mentioned but gave m.p. 87°. According to Pummerer, *et al.* (A. 1929, 1420) the alcohols are identical, have the  $C_{31}$  formula, and melt at 88°. Francis, Piper, and Malkin (Proc. Roy. Soc. 1930, [A], 128, 249) fractionated the acetate of the melissyl alcohol from carnauba wax and concluded that this alcohol is a mixture. Chibnall and collaborators (Biochem. J. 1934, 28, 2194) infer from melting-point data and X-ray analysis of mixtures of pure primary alcohols and from a similar examination of alcohols from waxes, that the wax products are mixtures, for which they deduce the probable compositions. Thus the melissyl alcohol, m.p. 87°, of Gascard and Damoy is formulated 40%  $C_{30}$ +40%  $C_{32}$ +20%  $C_{34}$ . They recommend that the names melissyl and myricyl be abandoned as they have always

been applied to mixtures and these should be distinguished by quoting their melting-points. On the other hand pure *n*-triacontanol,  $C_{30}H_{61}OH$ , m.p. 86.3–86.5°, has been isolated from the wax on lucerne leaves (Chibnall *et al.*, *ibid.* 1933, 27, 1885).

*Note.*—Misquotations in the literature. The formulations of Helduschka and Garels (*l.c.*, p. 298) are quoted in the inverse order by Francis *et al.*, *l.c.*, pp. 249, 250, and by Chibnall *et al.*, *Biochem. J.*, 1934, 28, 2198.

J. N. G.

**MYRISTICA FATS.** (NUTMEG BUTTER, VIOLA, OTOBA, etc., FATS.) This group comprises a number of fats, which are derived from the seeds of tropical trees of the Fam. Myristicaceae, and characterised by the presence of a very large proportion of (combined) saturated acids, and in particular of myristic (tetradecoic) acid: this acid may so preponderate that much of it appears in the fat in the form of the simple triglyceride *trimyristin*, accompanying mixed glycerides of myristic and other saturated and unsaturated acids.

Whilst they are of considerable scientific interest, most of the Myristica fats have little technical importance except in their countries of origin, where they are used by the native populations in pharmaceutical and cosmetic preparations (for external application), or for the manufacture of soap. Nutmeg butter, the best-known representative of the group, has also found application in Western Europe and N. America as a gentle local stimulant in hair lotions, plasters, etc., whilst Papuan nutmeg butter has acquired some eurrency as an adulterant or substitute for true nutmeg butter.

The Myristica fats are derived from the seeds (endosperm). As a rule, the crude fats are brownish or orange in colour (owing, probably, to colouring matters derived from the dark seed-coat, the infoldings of which spread deep into the endosperm) and contain considerable amounts of resinous and unsaponifiable constituents; in the case of a few members of the group, notably the true nutmeg, the seed, and the fat therefrom, contain appreciable quantities of aromatic essential oil.

In some species the "mace" or arillus of the seed also contains fat (*e.g.*, in *Pyncanthus kombo*), or, as in the nutmeg, essential oil, or both.

Nutmeg Butter, Mace Butter, is the yellowish or orange solid fat derived from the kernels of the true nutmeg, *Myristica officinalis* L. (Syn. *M. fragrans* Houtt, or *M. moschata* Thunb.) which is indigenous to the islands of the Indian Archipelago, notably, Molucca, the Banda Islands, Celebes, Sumatra, and Java, and is now cultivated there and also in the West Indies (Grenada), Brazil, and Guiana. Commercial nutmeg butter is recovered from undersized, damaged or worm-eaten seeds which are unsuitable for sale as spice. Formerly, all such defective seeds which could not be exported were worked up for the fat locally in the East Indies, by roasting or steaming, grinding and pressing. The brownish fat so obtained was exported in the form of bricks or bars wrapped in palm leaves, and was known in the trade as "Dutch" nutmeg butter, and in England as "soap of Banda." "Indian" mace butter was

of somewhat inferior quality. Of latter years, a considerable amount of mace-butter has been prepared in Holland by more refined methods of pressing from rejected seeds, or from seeds from which the essential oil of nutmeg has been previously recovered by distillation. About three-quarters of the total 38–40% of fat present in the seed is recovered in technical practice.

The analytical characteristics of commercial nutmeg butter vary considerably, owing, mainly, to the varying amounts of essential oil (4–25%) present, and to differences in the mode of preparation and purification of the fat. The following figures illustrate the usual ranges:  $\rho^{15}$  0.946–0.960;  $\rho^{100}$  0.884;  $n_D^{40}$  1.466–1.470 (G. S. Jamieson, "Vegetable Fats and Oils," 1942, p. 95); 1.470–1.475 (Utz, Chem. Rev. Fett- und Harz-Ind. 1903, 10, 11); sap. val. 168–180; iod. val. 45–59; m.p. 42–52°; titer 40–45°C. The free fatty acid content runs from 4–6% (calc. as myristic acid) and up to 20% of unsaponifiable matter may be present. The fatty acids of a purified sample of fat examined by Collin and Hilditch (*Biochem. J.* 1929, 23, 1281; J.S.C.I. 1930, 49, 141r), after elimination of the 19.5% of resinous matter present, consisted of: lauric 1.5, myristic 76.6, palmitic, 10.1, oleic 10.5, and linolic acid 1.3%. The true fat (glycerides) contained 71% of fully saturated glycerides (*i.e.*, 58.6% on the original purified, but still resinous, fat) of which about three-quarters consisted of the simple triglyceride *trimyristin* (*cf.* Bömer and Ebach, Z. Unters. Lebensm. 1928, 55, 511; Heiduschka and Häbel, Arch. Pharm. 1933, 271, 56. According to Power and Salway (J.C.S. 1908, 93, 1653), the unsaponifiable matter of nutmeg butter contains a substance  $C_{18}H_{22}O_6$ , some myristicin (3-methoxy-4:5-methylenedioxy-1-allylbenzene) and a very small amount of a phytosterol  $C_{20}H_{34}O$  (?), m.p. 134–135°.

Owing to its high content of combined myristic acid, nutmeg butter is practically completely soluble in 20–25 parts of boiling 95% alcohol; on cooling, the solution deposits crystals of trimyristin, m.p. 55° (*cf.* Utz, *l.c.*). Adulterants such as lard, petroleum jelly, etc., are not fully soluble in the hot spirit, and also lower the melting-point of the trimyristin precipitated on cooling; addition of waxes raises the melting-point of this fraction.

Nutmeg butter is not infrequently substituted or sophisticated by fats from other species of *Myristica*, and especially by Papuan nutmeg butter, from the seeds of the Papuan (New Guinea) long nutmeg, *M. argentea* Warb.; this fat is stated to have characteristics similar to those of true mace butter, but contains no, or very little, essential oil. The seeds of *M. malabarica* Lam. ("Bombay seeds" or "kai-phal," growing in Konkan, Kanara, Malabar, and Travancore, resemble nutmegs in appearance, but yield a fat of different character, which not only contains much more oleic acid than other *Myristica* fats, but also is anomalous among seed-fats in respect of its glyceride composition. A sample of the fat (18%) extracted by light petroleum from the kernels, and studied

by Collin (J.S.C.I. 1933, 52, 100r; cf. Collin and Hilditch, *ibid.* 1930, 49, 141r) contained about 15% of non-fatty resinous matter. The purified mixed fatty acids (iodine val. 53.6) consisted of: myristic 32, palmitic 16.9, stearic 3.2, oleic 47.4, and linoleic acid 0.5% by weight, *i.e.*, a molecular ratio of 1.3 mol. of saturated acids to 1 mol. of unsaturated acids: in a seed-fat of this composition, no fully saturated glycerides would be expected to be present, but in fact the fat was found to contain about 15% of fully-saturated glycerides, and it thus resembles laurel fat (Vol. VII, 195c) in being an exception among seed-fats to the general rule of "even distribution" of saturated and unsaturated acids in mixed glycerides.

Kombo Butter is derived from the seeds of *M. angolensis* Welw. (*Pycnanthus kombo* Baillon, Warb.), a tree (the "arbre à suif du Gabon") widely distributed in Gaboon. Kernels from Sierra Leone examined by Atherton and Meara (J.S.C.I. 1939, 58, 355) yielded 61.6% of a dark-brown fat containing considerable amounts of resinous matter, which was removed by means of sodium carbonate. The refined fat had an iodine value of 32.3 (cf. Anon., Bull. Imp. Inst. 1908, 6, 377) and its fatty acids were found to consist of: unsaponifiable matter 1.2, lauric 5.4, myristic 60.8, palmitic 3.6,  $\Delta^9$ -tetradecenoic 23.4, and oleic acid 5.6%. The occurrence of  $\Delta^9$ -tetradecenoic acid, apparently identical with the  $\Delta^9$ -myristoleic acid present in fish oils, whale oils, and butterfat, but hitherto unknown in vegetable oils, is remarkable.

The fat of *M. canarica* (iodine value ca. 27), the Indian "candle-nut tree" \* (cf. Hooper, Agric. Ledger, 1907, No. 3, 18) and Uchubá (*Bicuhyba* or *Urucuba*) Fat (iodine value 14; cf. Bolton and Hewer, Analyst, 1917, 42, 42) from *Virola bicuhyba* Humb.† have a high content of myristic acid, but have not been fully analysed by modern methods.

*Virola* Fat, from the kernels of the S. American (Brazilian) *Virola surinamensis* Warb. (*M. surinamensis* Roland) contains some 42% of trimyristin: the composition of the fatty acids of a sample examined by Atherton and Meara (J.S.C.I. 1939, 58, 353) was: caproic 0.5, lauric 14.9, myristic 73.2, palmitic 5.0, and oleic acid 6.4%. Steger and Van Loon (Rec. trav. chim. 1935, 54, 149) reported for "uchubá fat" from *Virola surinamensis*: lauric 12.6, myristic 63.0, palmitic 8.4, stearic 1.5, oleic 6.3, and linoleic acid 2.8% resinous matter 5.2%.

It is pointed out by T.P. Hilditch ("Chemical Constitution of the Natural Fats, 1st ed., 1940, p. 165) as a generalisation, that the seed-fats from species of *Virola* may contain from 10 to 20% of lauric acid, which distinguishes them from the fats of the allied genus *Myristica* in which, as a rule, very little, or no, lauric acid is

present: the content of myristic acid is about the same (70%) in both genera (cf. Verkade and Coops, Rec. trav. chim. 1927, 46, 528).

African Ochoco Fat (from *Scyphocephalum ochoco* Warb. Syn. *Ochocoa gabonii* Pierre) has an iodine value of about 2 and consists almost entirely of trimyristin (cf. J. Lewkowitsch, Analyst, 1908, 33, 313; Margailan, Ann. Mus. Col. Marseille, 1929, [iv], 7, No. 3, 5-32).

Otoba Butter, American Nutmeg or Mace Butter (also known commercially as "otoba wax"), iodine value 54, from the seeds of *M. otoba* Humb. and Bonp., a native of Colombia, where the fat is used in the treatment of skin diseases of domestic animals, is of the same type as other *Myristica* fats (cf. Anon., Bull. Imp. Inst. 1920, 18, 168). A sample analysed by Baughman, Jamieson, and Brauns (J.A.C.S. 1921, 43, 199) contained 9.3% of volatile oil (mainly sesquiterpenes) and 20.4% of unsaponifiable matter including a substance *otobite*,  $C_{20}H_{36}O_2$  (m.p. 137-138°C.,  $[\alpha]_D +35.7^\circ$ , cf. Uricoechea, Annalen, 1854, 91, 369) and its isomeride, *iso-otobite* (m.p. 106-108°C.,  $[\alpha]_D +5.3^\circ$ ). The fatty acids, freed from unsaponifiable matter, consisted of lauric 20.8, myristic 73.4, palmitic 0.3, and oleic acid 5.5%.

Both *otobite* and *iso-otobite* yield pentabromides, and give an intense and persistent pale red coloration with sulphuric acid.

It may be noted that several of the *Myristica* fats, notably *bicuhyba* fat and the fat of *M. canarica*, are stated to develop a blood-red colour on treatment with concentrated sulphuric acid.

E. L.

MYROBALANS (v. Vol. IV, 276d; VII, 267b).

MYROSIN (v. Vol. IV, 314b).

MYRRH. *Herabol myrrh*. *Heerabol-myrrha* is an oleo-gum-resin, the spontaneous exudate of the small tree *Commiphora molmol* Engl. (Fam. Burseraceae) and possibly of other species of *Commiphora*, inhabitants of the Somali and Arabian littoral of the Red Sea. Nomad tribes collect the hardened drops of exudate which adhere together forming rounded, brittle, translucent masses of a red-brown colour and dusty surface. The drug, which has an agreeable odour and a strongly bitter taste, is shipped from Aden as Somali myrrh or herabol myrrh; it is sorted by European merchants into best quality or "electa" and second quality or "naturalis." Together with *olibanum*, myrrh has been used as a constituent of incense from the earliest times. The Egyptians employed it not only in fumigations and in embalming, but also in medicine, and it has retained its place in modern pharmacopœias.

The composition of the drug varies considerably as shown by the data given in B.P.C. 1934, 663: gum 57-61%, resin 25-40%, volatile oil 2.5-8%, impurities 3-4% (cf. Tschirch and Stock, "Die Harze," 1935, II, 1, 218). British Pharmacopœia, 1932, 290, specifies: not more than 70% insoluble in 90% alcohol, ash not to exceed 9% and not more than 4% foreign organic matter. Genuine myrrh gives the following reaction which is not obtained with *bisabol myrrh* or with *bdellium* (Vol. I, 658c)

\* This tree must not be confused with *Aleurites moluccana* of the Philippine Islands, etc., the seeds of which furnish the well-known drying oil, candle-nut (lumbang) oil (v. Vol. II, 282b).

† Uncertainty exists as to the botanical original of the uchubá and bicuhyba fats and some other minor myristica fats examined by various investigators. Cf. Le Cointe, "Apontamentos sobre as sementes oleaginosas de florastas amazonicas," Rio de Janeiro, 1931; Steger and Van Loon, Rec. trav. Chim. 1935, 54, 149.



which are known adulterants: an ethereal extract of the sample is evaporated and the residue exposed to bromine vapour when a violet colour is developed. Quantitative determinations may serve the same purpose. Although variable, the ester value, ca. 204, and the saponification value, ca. 229, of *heerabol myrrh* differ markedly from the corresponding values, ca. 125 and 145, of *bisabol myrrh* and also from those of African *bdellium*, 69-96 and 79-117 respectively (Tschirch and Stock, *op. cit.*, p. 225).

**Composition of Myrrh.**—O. von Friedrichs (Arch. Pharm. 1907, 245, 427) continued the work of Tschirch and Bergmann (*ibid.* 1905, 243, 611) and separated a number of amorphous constituents: two bivalent phenols  $\alpha$ -*heerabolmyrrhol*, m.p. 248-250°, and  $\beta$ -*heerabolmyrrhol*, m.p. 168°; a resin, *heeraboresen*, m.p. 100-102°, insoluble in alkalis and light petroleum; four acids separated from the ether-soluble fraction were  $\alpha$ -,  $\beta$ -, and  $\gamma$ -*commiphoric acid*, m.p.'s 201°, 205°, 169-172°, respectively, and *commiphoric acid*, m.p. 135°. The ether-insoluble fraction yielded two acids  $\alpha$ - and  $\beta$ -*myrrhololic acid*, m.p.'s 220-225°, and 187-190°, respectively.

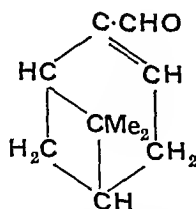
**Oil of Myrrh**, a viscous yellowish-green liquid with a strong odour of myrrh, has  $\rho$  1.011,  $[\alpha]_D$  -73.9°,  $n_D^{20}$  1.5359, acid value 6.15, ester value 47.6. The oil contains *m*-cresol, cuminaldehyde, cinnamaldehyde, *myrrholic acid*, *heerabolene*,  $C_{15}H_{24}$  (von Friedrichs, *l.c.*), pinene, dipentene, limonene, eugenol (cf. Gildemeister and Hoffmann, "Die ätherischen Öle," 1931, III, 161; Lewinsohn, Arch. Pharm. 1906, 244, 412).

**Gum.**—A white emulsion is formed when the drug is triturated with water. The gum has  $[\alpha]_D$  +23.8° for a 2% aqueous solution (von Friedrichs, *l.c.*). Oxidation with nitric acid yields mucic acid. Hydrolysis gives arabinose, galactose, and xylose. An oxidase is associated with the gum.

**Burseracin**, 1.5-2.5% in myrrh, an astringent amorphous substance (G.P. 550583) has been recommended for treating wounds.

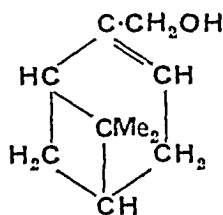
**Medical Properties.**—Myrrh is prescribed as a stomachic and carminative and as an expectorant in catarrhs. The diluted tincture is used alone or with borax in mouth washes. According to Gatti and Gayola (Amer. Chem. Abstr. 1923, 17, 2150) oil of myrrh is inferior to the oils of eucalyptus, pine, and myrtle in the treatment of pulmonary diseases. For the pharmacology of myrrh, see Macht and Bryan, Amer. J. Pharm. 1935, 107, 500.

J. N. G.

**d-MYRTENOL,**

b.p. 91.75°/12.5 mm.,  $\rho_4^{20}$  0.9898,  $[\alpha]_D$  +15.68°, occurs in false camphor weed oil from the weed of *Hernandia peltata* (see TERPENES).

J. L. S.

**d-MYRTENOL,**

b.p. 218°/771 mm., 103-104°/11 mm.,  $\rho_{15}^{18}$  0.981,  $n_D$  1.4951,  $a_D$  +45°, occurs in the essential oil from the leaves and flowers of *Myrtus communis* L. (oil of myrtle) and in the oil from the shrub *Darwinia grandiflora* (see TERPENES).

J. L. S.

**MYRTICOLORIN** (v. Vol. IV, 391a; VI, 92b).

**MYRTILLIDIN**, a mixture of anthocyanidins obtained by the hydrolysis of myrtillin (v. *infra*).

W. B.

**MYRTILLIN.** This name was given by Willstätter and Zollinger (Annalen, 1915, 408, 103) to a crystalline and apparently homogeneous and distinct anthocyanin, which they isolated from fresh, undried skins of bilberries (Heidelbeeren, *Vaccinium myrtillus* L.). The chloride was assigned the composition  $C_{22}H_{23}O_{12}Cl \cdot 4H_2O$ . Further work (*ibid.* 1917, 412, 195) led to the conclusion that myrtillin was a galactoside of a monomethyl delphinidin. Karrer and Widmer (Helv. Chim. Acta, 1927, 10, 5) and Bell and Robinson (J.C.S. 1934, 136, 813) have shown, however, that the bilberry pigment is a complex mixture of anthocyanins in which a monoglucoside and a monogalactoside of delphinidin, a malvidin monoglucoside and a petunidin monoglycoside are present. Reynolds and Robinson (*ibid.* 1934, 136, 1039) consider that the delphinidin glucoside is almost certainly the 3- $\beta$ -glucoside, since all the monoglucosidic anthocyanins of natural origin so far isolated (callistephin, chrysanthemin, oxycoccicyanin, and oenin) belong to this type. They propose the name myrtillin-a for the glucoside, and myrtillin-b for the galactoside of delphinidin which occur in the skins of bilberries.

W. B.

**MYRTLE OIL. MYRTOL.** Myrtle oil is obtained by steam distillation of the leaves of *Myrtus communis* (Fam. Myrtaceae) which grows abundantly in Mediterranean countries. The yellow or greenish-yellow oil, with a refreshing odour due to myrtonyl esters, is obtained in about 0.3% yield. It also contains pinene, cineole, camphor, camphene, and traces of aldehydes. It is a reputed remedy in pulmonary diseases. Analytical results for the oil over a period of ten years have been summarised:  $\rho_{15}^{18}$  0.8792-0.8912,  $a_D$  +24° 30' to +28° 48',  $n_D^{20}$  1.466-1.469, acid value (max.) 2.8, ester value 42.7-59.5, esters (as  $C_{15}H_{20}O_2$ ) 14.95-20.8%, ester value after acetylation 88.3-105.7, soluble in 0.2-1.5 vol. of 90% alcohol (Etabl. Antaine Chiris, Parfums de France, 1935, 13, 239; Amer. Chem. Abstr. 1936, 30, 246).

**Myrtol.**—The fraction of myrtle oil boiling at



160–180° contains esters of *myrtenol* (this Vol., p. 261c) and was formerly extensively prescribed under the trade name "*Myrtol*" for diseases of the lungs. Later its efficacy was questioned, and according to Gatti and Gayola (*ibid.* 1923, 17, 2150) myrtle oil is inferior in therapeutic value to the oils of eucalyptus and pine.

J. N. G.

**MYRTLE WAX**, *Myrtle berry wax*, *Laurel wax*, *Bayberry wax*, *Cape berry wax*, is obtained from the fruit of *Myrica* spp. (Fam. Myricaceæ) chiefly from *M. cerifera* in North America, *M. cordifolia* in Cape Colony and *M. jalapensis* in Mexico. The wax is obtained in 20% yield by boiling the berries with water. The description "wax" is a misnomer since the substance is a fat consisting chiefly of *palmitin* which is obtained in a pure state by crystallising four times from light petroleum (Smith and Wade, J. Amer. Chem. Soc. 1903, 25, 629). The wax has m.p. 48°,  $\rho_{15.5}^{99}$  0.878, sap. value 217, iodine value 3.9 (Smith and Wade, l.c.). The Mexican wax (*supra*) gave m.p. 43.2°,  $\rho_{15}^{99}$  0.8763, sap. value 214.5, iodine value 2.38, acid value 4.07 (Olsson-Seffer, Bull. Imp. Inst. 1909, 7, 411). The wax is used as an ingredient of candle wax and of polishes for leather.

J. N. G.

**MYTILITOL**, methylcyclohexanexol,



is a crystalline cyclose obtained in 0.015% yield from the flesh of the common sea mussel, *Mytilus edulis* (Ackermann, Ber. 1921, 54 [B], 1938). It has m.p. 272°, is only slightly soluble in cold water and is insoluble in the usual organic solvents; it has a faintly sweet taste, is optically inactive, and does not reduce ammoniacal silver nitrate or Fehling's solution (Daniel and Doran, Biochem. J. 1926, 20, 676).

J. N. G.

**MYXOXANTHIN** (v. Vol. II, 400d).

**NAADSTEENEN** (v. Vol. III, 573c).

**NACRITE** (v. Vol. III, 196a).

**NAGA RED**, *Nagana Red*, is a benzopurpurin dyestuff, the sodium salt of benzidine-disazo-bis-2-naphthylamine-3:6-disulphonic acid, proposed as a trypanocide for the treatment of the African cattle disease "nagana," but was effective only *in vitro* (Ehrlich and Hata, "Experimental Chemotherapy of Spirillooses," London, 1911).

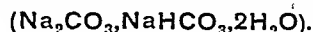
J. N. G.

**NAGYAGITE**. A sulpho-telluride of lead and gold, of uncertain formula, probably  $Pb_5Au(Te,Sb)_4S_{5-8}$ . It contains approximately Pb 54, Te 20, S 10, Au 8, Sb 6%, with small amounts of silver and selenium. The crystal form may be monoclinic, though the X-ray elements have recently been stated in terms of a tetragonal cell. It occurs as thin tabular crystals and foliated masses, the perfect cleavage flakes being flexible and slightly malleable, with a blackish lead-grey colour and splendid lustre. Hence popularly called "foliated tellurium" and "black tellurium." Hardness 1–1½,  $\rho$  7.4. An uncommon mineral, formerly found in some abundance in Tran-

sylvania at Nagyág, and also reported from Kalgoorlie in Western Australia, New Zealand, and various localities in the United States and elsewhere.

D. W.

**NAHCOLITE**. Sodium carbonate minerals include thermonatrite ( $Na_2CO_3 \cdot H_2O$ ), natron ( $Na_2CO_3 \cdot 10H_2O$ ), and trona



The bicarbonate ( $NaHCO_3$ ), named nahcolite from the formula, has recently been recognised in the presence of free carbon dioxide or of calcium bicarbonate solutions; in the dry salt lake of Little Magadi in Kenya Colony (Walther, Amer. Min. 1922, 7, 86); in an ancient Roman conduit near Naples (Bannister, Min. Mag. 1929, 22, 53); and in some abundance in bores in the salt crust of Searles Lake in California (Foshag, Amer. Min. 1940, 25, 769).

L. J. S.

**NAIL-HEAD SPAR** (v. Vol. VI, 203c).

**NAMARA POTATO** (v. Vol. I, 497a).

**NANDININE** (v. Vol. IV, 55a).

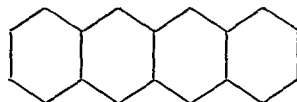
**NANKIN** (v. Vol. I, 133b).

**NAPHTHA**, a term frequently applied to various mixtures of volatile hydrocarbons obtained by fractional distillation of petroleum or by destructive distillation of coal, lignite, peat, and shale, although wood naphtha (Vol. I, 183d; III, 558a) is crude methyl alcohol (this Vol., p. 12c). The chief uses of the hydrocarbon naphthas are as solvents and diluents in the varnish, paint, and lacquer industries (Vol. II, 472a). *Coal tar naphtha* (Vol. III, 211b, 214b). *Light solvent naphtha*, boiling range (b.r.) 110–160°, contains toluene and the xylenes. *Heavy naphtha*, b.r. 160–190°, contains alkyl xylenes, coumarone, and indene and is used in the manufacture of synthetic resin (Vol. III, 413b). [For toxicity of solvent naphtha, see Taylor, Chem. and Ind. 1939, 17, 1078.] *Petroleum naphtha*. Light naphtha, b.r. 90% below 125°; V.M.P. naphtha or varnish makers' and painters' naphtha in the United States, "X44 spirit" in England, b.r. 100–160°. Heavy naphtha, turpentine substitute, b.r. 90% below 200°.

For solvent properties of naphthas, see T. H. Durrans, "Solvents," 4th ed., London, 1938; I. Mellan, "Industrial Solvents," New York, 1939; for toxicity, v. *supra*, and "Toxicity of Industrial Organic Solvents," Industrial Health Research Board, Report No. 80, 1937, H.M. Stationery Office.

J. N. G.

**NAPHTHACENE**,



Naphthacene, 2:3-benzanthracene, tetracene,

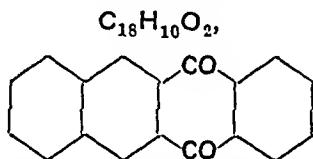


is contained in the highest boiling fractions of coal tar (Coulson, J.C.S. 1934, 1406) and is identical with the yellow impurity in commercial anthracene which had been named chrysogen and crackene Vol. I, 385a; III,

119c). Naphthacene forms bright orange plates or filaments, m.p. 357° (Dufraisse and Horclois, Bull. Soc. chim. 1936, [v], 3, 1873). When heated above 300° it sublimes, forming a greenish-yellow vapour. It is insoluble in benzene but dissolves in sulphuric acid, forming a moss-green solution. Oxidation with fuming nitric acid gives naphthacenequinone (*v. infra*). The colourless photo-oxido,  $C_{18}H_{12}O_2$ , is formed on exposing a solution in carbon disulphide to oxygen and light. A similar behaviour is shown by anthracene and by aryl-naphthalenes, coloured hydrocarbons classified as *rubenes*. The photo-oxido of 5:6:11:12-tetraphenyl-naphthalene, *rubrene*, emits light and evolves oxygen when heated, regenerating the parent hydrocarbon (Kon, Chem. Soc. Annual Rep. 1932, 29, 176; Cook, *ibid.* 1942, 39, 188; Bergmann and McLean, Chemical Reviews, 1941, 28, 388). Clar has prepared the linear benzologues of naphthacene: *pentacene*, deep blue (Ber. 1930, 63 [B], 2967), *hexacene*, deep green (*ibid.* 1939, 72 [B], 1817; 1942, 75 [B], 1286), *heptacene*, almost black, green in thin layers (*ibid.*, p. 1330).

J. N. G.

NAPHTHACENEQUINONE, 2:3-benz-anthraquinone, 2:3-phthaloylnaphthalene,



Yellow needles, m.p. 294° from nitrobenzene, is only slightly soluble in the usual organic solvents but dissolves in sulphuric acid giving a reddish-violet solution. It is prepared by oxidation with litharge at 330° of tetramethylene-2:3-anthraquinone obtained by condensing phthalic anhydride with tetralin. Reduction by passage over zinc dust gives naphthacene (*v. supra*). For alternative methods, see Fieser, J. Amer. Chem. Soc. 1931, 53, 2329; Waldmann and Mathiowetz, Ber. 1931, 64 [B], 1713). The preparation of derivatives was described in a series of papers by Weizmann *et al.*, J.C.S. 1903-1909. Clar has discussed the absorption spectra and reactivities of naphthacenequinone and its derivatives (Ber. 1936, 69 [B], 607; 1940, 73 [B], 81, 596). A yellow vat-dyestuff, 1-benzamido-2:3-benzanthraquinone, was prepared by Waldmann and Polak (A. 1938, II, 104).

J. N. G.

## NAPHTHALENE.

*Introduction.*—This article is divided into three main parts:

- (I) Naphthalene and its derivatives (*v. infra*).
- (II) Alkyl-naphthalenes and their derivatives (p. 389a).
- (III) Hydrogenated naphthalenes and their derivatives (p. 409b).

A synopsis of each branch of the subject is given at the beginning of the appropriate part. The following abbreviations are employed for the names of firms to which frequent reference is made in the text of this article:

Aktienges.	Aktien-Gesellschaft für Anilinfabrikation in Berlin.
B.D.C.	British Dyestuffs Corporation, Ltd.
Badische	Badische Anilin- und Soda-Fabrik in Ludwigshafen a. Rh.
Bayer	Farbenfabriken vorm. F. Bayer & Co. in Elberfeld.
Bindsch.	Basler chemischer Fabrik, vorm. Basler chem. Fabrik Bindschedler in Basel.
Brönner	Farbfabrik vorm. Brönner in Frankfurt a. M.
Cassella	Anilinfarbenfabrik von L. Cassella & Co. in Frankfurt a. M.
Dahl	Dahl & Co. in Barmen.
Du Pont	E. I. Du Pont de Nemours & Co.
Geigy	Anilinfarben- und Extrakt-Fabriken vorm. J. R. Geigy in Basel.
Gesellsch.	Gesellschaft für chemische Industrie in Basel.
Griesheim	Chemische Fabrik Griesheim-Elektron in Frankfurt a. M.
Heyden	Chemische Fabrik von Heyden, Aktiengesellschaft in Radebeul bei Dresden.
Höchst	Farbwerke vorm. Meister, Lucius und Brüning in Höchst a. M.
I.C.I.	Imperial Chemical Industries, Ltd.
I.G.	Interessengemeinschaft der Farbenindustrie Akt. Ges.
Kalle	Kalle & Co. Aktiengesellschaft in Bielefeld a. Rh.
Landshoff	Chemische Fabrik Grünau, Landshoff und Meyer.
Leonhardt	Farbwerk Mühlheim vorm. A. Leonhardt & Co. in Mühlheim bei Frankfurt.
Sandoz	Chemische Fabrik vorm. Sandoz in Basel.
Schüllkopf	Schüllkopf Anilin and Chemical Co., Buffalo (U.S.A.).
Verela	Vereln chemischer Fabriken in Mannheim.

## PART I. NAPHTHALENE AND ITS DERIVATIVES.

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### Introduction.

Naphthalene,  $C_{10}H_8$ , is one of the most important hydrocarbons of the aromatic series. It is present in crude coal gas and is formed abundantly in the distillation of coal tar, this being the main commercial source of supply although some may be obtained from petroleum cracking. It had little technical importance until the discovery, dating from about 1876, of the value of its derivatives, naphthylamines, naphthols, and their sulphonic acids, as intermediates for the manufacture of dyes. Since then intense effort has been devoted to the study of naphthalene and its derivatives, many of which have become of great technical importance. In the field of naphthalene chemistry academic and technical progress have been and still are so interdependent that, for technical purposes, any account of the subject needs to be as complete as possible on both sides. Nevertheless the amount of research which has been done is so extensive that much has had to be omitted from this account or dismissed with the briefest reference.

**Historical.**—The production of naphthalene in the manufacture of coal gas seems to have been noticed first by Clegg (cf. Brande, Quart. Journ. Sci. 1820, 8, 287); its discovery in coal tar, however, was made in 1819 simultaneously by Garden (Annals. Phil. 1820, 15, 74) and Brande (i.e.), the latter regarding it as a hydrocarbon (cf. Thomson, Schweig. J. 47, 337). It was further examined by Kidd, who named it "naphthaline" (Phil. Trans. 1821, 209), by Ure (*ibid.* 1822, 473), and by Chamberlain (Annals. Phil. 1823, [ii], 6, 135). Its composition was first determined by Faraday during his investigation of its isomeric monosulphonic acids (Phil. Trans. 1826, 159) and later by Laurent (Annalen, 1832, 3, 11).

**Formation and Sources.**—Naphthalene is a usual constituent of the products obtained by heating organic substances at comparatively high temperature. Thus, methane or acetylene (Berthelot, Bull. Soc. chim. 1867, [ii], 7, 306), alcohol or acetic acid (Berthelot, Ann. Chim. Phys. 1851, [iii], 33, 295) or toluene, xylene, and cumene or a mixture of benzene or styrene with ethylene (Berthelot, Compt. rend. 1866, 63, 790, 834; Bull. Soc. chim. 1866, [ii], 6, 268; 1867, [ii], 7, 218, 278, 285) passed through a red-hot tube filled with pumice give some naphthalene. Further work on the same lines has been done by Ferko (Ber. 1887, 20, 660), Graebe

(*ibid.* 1874, 7, 49), Lorenz (*ibid.* 1874, 7, 1097), and Carnelley (J.C.S. 1880, 37, 705).

Similarly passing the residues of Baku petroleum through a red-hot tube gave some naphthalene (Rudnew, Dingers polytech. J. 1881, 239, 72; and earlier workers). In a similar way naphthalene has been obtained from the oils of brown coal tar (Liebermann and Burg, Ber. 1878, 11, 723) and pinewood tar (Atterberg, *ibid.* 1878, 11, 1222). According to Cosçing (Petroleum, 1935, 31, 5) naphthalene is present in crude Rumanian oil.

Naphthalene is present in oil-gas tar (Armstrong and Miller, J.C.S. 1886, 49, 80), but its main source is in the tar produced by the high-temperature carbonisation of coal in the manufacture of gas and coke. It is not a normal constituent of tar from low-temperature carbonisation, though naphthalene has been found in the primary tar from Dalton Main coal carbonised at 450° (Morgan, Fuel, 1931, 10, 183). Morgan (J.S.C.I. 1932, 51, 75*r*) found that carbonisation of a coal at 625° gave tar containing only a trace of naphthalene whereas the same coal carbonised at 1,350° in a horizontal retort gave a tar containing 7.1% naphthalene in the dry tar. The same coal carbonised at 1,260° in a vertical retort gave a tar containing only 3.3% of naphthalene. Comparing horizontal and vertical retorts, Holmquist (Gas- u. Wasserfach, 1932, 75, 700) found that while with horizontal retorts the naphthalene was 30 g. per 100 cu.m. of gas, with vertical retorts it was only 13 g.

From a study of the equilibria of aromatic hydrocarbons from the cracking of petroleum it has been concluded that naphthalene makes its appearance at the point where the toluene-xylene content passes its maximum (Rittmann and Twomey, Ind. Eng. Chem. 1916, 8, 20), the temperature at which it first appeared being 750° with a gas oil obtained in refining crude Pennsylvanian petroleum (Egloff and Twomey, J. Physical Chem. 1916, 20, 145). Kosaka and Oshima (B. 1927, 691) have concluded that the naphthalene of high-temperature coal tars is largely produced by the decomposition and recombination of phenolic compounds. The thermal decomposition of a coal tar obtained by distilling coal *in vacuo* at 450° has been studied by Jones (J.S.C.I. 1917, 36, 5), who found that the higher olefins are at a maximum at 500° but at 750° these have practically disappeared, their disappearance coinciding with the appearance of naphthalene.

In addition to appearing in coal tar naphthalene naturally contaminates coal gas and, unless the amount is effectively reduced, it leads to blockage of pipes in cold weather. The coal gas must therefore be washed with a solvent. Schuster (Gas- u. Wasserfach. 1932, 75, 693) states that tetralin is an excellent solvent for this purpose and has been used in one plant for several years. Verein Stahlwerke (B.P. 366712) claim the use of a mist of water to separate naphthalene from gas while N. V. Silica en Ovenbouw Mij. (B.P. 337723) introduce a solvent into the gas stream which then passes through an electrical precipitator when the solvent containing the naphthalene is precipitated.

Synthetic methods of preparing naphthaleno have been described by Aronheim (Ber. 1873, 6, 67) Wreden and Znatowicz (*ibid.* 1876, 9, 1606), and Baeyer and Perkin (*ibid.* 1884, 17, 448). According to Bradley and Jacobs (B.P. 26061, 1898) naphthalene is formed by heating barium carbido with barium hydroxide at 800-1,000°.

*Isolation and Purification.*—Naphthaleno occurs in the "light oil" (b.p. 110-210°) and "creosote oil" (b.p. 210-240°) but most abundantly in the intermediate fraction, "carbolic oil" (b.p. 240-270°) of the tar distiller. Naphthaleno crystallises out on cooling the "carbolic oil" and is separated by draining and the crystals further purified by hydraulic pressing at 50-60°, the resulting product in the form of round cakes usually of a grey colour being known as "hot pressed naphthalene." The hot pressed naphthalene before being used for any chemical purpose is usually purified by treatment with sulphuric acid, removal of acid by water and caustic soda and finally fractional distillation. A good account of this treatment is given by Skopnik (Chem.-Ztg. 1927, 51, 211) and G. T. Morgan and J. D. Pratt, "British Chemical Industry," London, Edward Arnold and Co., 1938, p. 217). The tar-oil fraction is redistilled and the naphthalene allowed to crystallise slowly, the crystals are well drained and then hot pressed at 50-60° at a pressure of 300 atm. The crude naphthaleno (m.p. 79-79.1°) is melted and washed hot, first with 1% by weight of sulphuric acid ( $\rho$  1.70) to remove moisture and secondly with 3% by weight of sulphuric acid ( $\rho$  1.84) to polymerise impurities. After washing with water and finally with caustic soda the naphthalene is fractionally distilled under vacuum. The first runnings are returned for further treatment and the main fraction collected having m.p. 79.9°. This product should give no coloration on melting with an equal volume of concentrated sulphuric acid or on standing for 2 hours over concentrated nitric acid. According to Ozerski (B. 1936, 970) the losses on purification are usually 3-6% by hot pressing, 5-8% by washing, and 4-8% by rectification.

There are numerous patents dealing with minor variations on the above scheme of purification. Many other methods have also been proposed, e.g., by treatment with air or oxygen (Ges. für Teerverwertung m.b.H., G.P. 277110; Rütgerswerke A.-G., B.P. 505742), treatment with ferric chloride (Oborschlesische Koksworko, and Chem. Fabr. A.-G., F.P. 583270), with aluminium chloride (Ges. für Teerverwertung, G.P.a. 47397), and by crystallisation from hydro-naphthalenes (Kutschenrouter, G.P. 317634).

A more highly purified naphthalene is required for the hydrogenation of naphthaleno or for production of nitronaphthalene for catalytic reduction to  $\alpha$ -naphthylamine since it is necessary to remove catalyst poisons, particularly sulphur compounds (v. Tetralin, this Vol., p. 413c).

*Properties.*—Naphthalene purified by crystallisation from ether has m.p. 80.21-80.23° (Do Beule, Bull. Soc. chim. Belg. 1931, 40, 195). Finck and Wilhelm have determined the b.p. at

760 mm. as 217.95° and have determined the formula for the effect of pressure over the range 700-800 mm. (J. Amer. Chem. Soc. 1925, 47, 1577). The heat of evaporation of naphthaleno is 18,280 g.-cal. per mol. (Andrews, J. Physical Chem. 1926, 30, 1497). The heat of combustion is variously given as 9,613.7 g.-cal. (Schläpfer and Fioroni, Helv. Chim. Acta, 1923, 6, 713); 9,614.2 g.-cal. (Keffler and Guthrie, J. Physical Chem. 1927, 31, 58); 9,603 g.-cal. (Keffler, J. Chim. phys. 1931, 28, 457). The molal latent heat of fusion is calculated from solubility determinations as 4,440 g.-cal. (Sunier and Rosenblum, J. Physical Chem. 1928, 32, 1049). Kolossovsky (Bull. Soc. chim. Belg. 1925, 34, 221) determined the difference between the real and apparent molecular heat of naphthalene in a number of solvents. The critical temperature of naphthalene is 476.5° (Shuravlev, J. Phys. Chem. Russ. 1937, 9, 875).

The solubility of naphthaleno in methyl, ethyl, propyl, and butyl alcohols between 20° and 70° has been determined, the solubility increasing in this order (Sunier, J. Physical Chem. 1930, 34, 2582). The solubility in benzene (100 parts) is 30.02 at 0° and 85.5 at 31°; in toluene 23.5 at 0° and 77.1 at 33°; in xylene 18.92 at 0°, 67.05 at 33°, and 90.06 at 41° (Schläpfer and Flachs, Helv. Chim. Acta, 1927, 10, 381; cf. Rhodes and Eisenhauer, Ind. Eng. Chem. 1927, 19, 414). The coefficient of solubility of naphthalene vapour in tetralin has been determined by Mauras (Bull. Soc. chim. 1937, [v], 4, 49). Weissenberger (Z. angew. Chem. 1927, 40, 776) gives the solubility data for naphthalene in tetralin, hexalin, methylhexalin, and decalin at various temperatures up to 50°. In tetralin the solubility in g. per 100 g. solvent is 50 g. at 30°, 37 g. at 20°, 27 g. at 10°, and 19 g. at 0°. Colloidal solutions of naphthaleno can be formed in aqueous sucrose (Weimann, Kolloid-Z. 1930, 51, 100). Naphthaleno volatilises at temperatures considerably below its boiling-point. It is readily volatile in steam and Naumann (Ber. 1877, 10, 2016; 1878, 11, 33) has determined the relevant data at 759.5, 757, and 733 mm. pressure. At 759.5 mm. the temperature of the liquid is 97.8°, of the vapour 99.2°, and the ratio of distilled naphthaleno to water is 100:520. Andrews (J. Physical Chem. 1926, 30, 1497) has determined the vapour pressure of naphthaleno at low temperatures. Barker (Z. physikal. Chem. 1910, 71, 235) gives the vapour pressure of naphthaleno as 0.064 mm. at 20°, 7.4 mm. at 80°, and 18.5 mm. at 100°.

*Tests.*—Naphthaleno is usually purchased either as crude "hot pressed" material or as the purified product. The quality of the "hot pressed" material is typified by the following specification: c.p. not below 77.5°, residue on ignition not above 0.2%, residue on volatilisation at 250° not above 0.3%, and moisture not above 1%. Pure naphthaleno of a quality normally used in manufacture is typified by the following specification: c.p. not below 79.6°, moisture not more than 0.2%, and the coloration with hot sulphuric acid not more than a faint pink. A detailed description of the analysis of naphthaleno is given in Lungo and Keano's "Technical Methods of Chemical Analysis," Vol. IV (2nd ed.).

The coloration of naphthalene with hot concentrated sulphuric acid may be defined against colour standard solutions made from cobaltous nitrate and sodium sulphide. Another colour test is that the material exposed to the vapour of concentrated nitric acid should not show discoloration during 2 hours.

**Analysis.**—The determination of naphthalene in coal gas or the various tar-oil fractions is usually made by methods dependent on the formation of the sparingly soluble picrate. As a qualitative test this will detect as little as 1 mg. of naphthalene. There is a considerable literature on the estimation of naphthalene in coal gas and an account of several picrate methods is given in Lunge and Keane's "Technical Methods of Chemical Analysis." The picrate method of Colman and Smith (J.S.C.I. 1900, 19, 128) was modified by Jorissen and Rutten (*ibid.* 1909, 28, 1179). Modifications of the method are given by Seebaum and Oppelt (Gas- u. Wasserfach, 1934, 77, 280), Knublauch (Gas J. 1917, 137, 61; J.S.C.I. 1917, 36, 702), and Walters (*ibid.* 1926, 45, 205r). U.G.T. Contracting Co. (U.S.P. 1443330; 1678591) propose a method in which coal gas is passed through a standard solution of picric acid and the usage of picric acid determined by the increase in electrical resistance of the solution.

For the determination of naphthalene in tar-oil, Mezger (Gas- u. Wasserfach, 1921, 64, 413 and 722) passes purified coal gas through the oil in presence of dilute phosphoric acid at 65–70° and absorbs the volatilised naphthalene in picric acid solution. Alternatively, the tar-oil may be shaken with picric acid solution and the excess of picric acid determined in the filtrate (Shdanov and Zelvjanskaja, B. 1940, 510). Kirby (J.S.C.I. 1940, 59, 168) describes the procedure for determining naphthalene in all grades of creosote salts and tar-oils.

Calcott, English, and Downing (Ind. Eng. Chem. 1924, 16, 27) determine the naphthalene content of crude naphthalene by volatilisation from caustic soda, sulphonation of the volatilised product and oxidation with vanadic acid, the excess of the latter being titrated with permanganate.

The moisture in naphthalene may be determined by the Dean and Stark method of distillation with xylene, or by the change in the critical solution temperature of a standard toluene–water mixture after addition of the moist naphthalene (Calcott, English, and Downing, *l.c.*).

**Production.**—During the decade preceding the outbreak of war in 1939 there had been a rapidly growing demand for naphthalene, and a corresponding increase in production. This increased demand was mainly due to the rapidly expanding use of phthalic acid and its anhydride for the manufacture of synthetic resins and of phthalic esters for use as plasticisers, the phthalic acid being exclusively manufactured from naphthalene. Great Britain in 1929 produced about 18,480 tons, and in 1936 the amount had increased to 31,250 tons. Exports in the latter year were about 11,750 tons, of which about 6,000 tons went to the U.S.A. Figures for production and use of naphthalene in the U.S.A.

are given in the United States Tariff Commission Report No. 131, 2nd Series, 1938, on "Synthetic Resins and their Raw Materials." Production in 1937 is given as 115,979,000 lb. of crude and 52,194,000 lb. of refined naphthalene, the selling price being 0.06 dollars per lb. The U.S.A. imported a further 52,664,277 lb. of crude.

The world production of naphthalene in 1936 was estimated at 200,000–210,000 metric tons (*see Chem. Ind.* 1938, 61, 27). Germany then was still the world's largest producer, although her share of the total production had fallen from 40% in 1929 to 25% in 1936. Great Britain and the United States were each responsible for 18–20% of the total. For further details of the production, imports, and exports of naphthalene by different countries, the references given should be consulted.

**Uses.**—The most important outlets for naphthalene are in the dyestuffs industry and the manufacture of phthalic anhydride for synthetic resins. It is also used in the manufacture of lampblack, as an addition to enrich illuminating gas and motor fuel, and as an insecticide and soil fumigant. Chlorinated naphthalenes find use as synthetic waxes, valuable on account of their dielectric properties. Although the study of naphthalene chemistry is usually associated with the dyestuffs industry, during more recent times the products of that study have been finding applications in other directions, for instance, in medicinal substances and to an important extent in rubber preservatives. Some of these uses are as follows:

In the *rubber industry* phenyl- $\alpha$ -naphthylamine and phenyl- $\beta$ -naphthylamine have considerable use as "anti-agers" (Goodyear, B.P. 281616). *p*-Hydroxy- and *p*-ethoxy-phenyl- $\beta$ -naphthylamine has also been proposed as a rubber "anti-ager" (Du Pont, B.P. 428146; Wingfoot Corporation, U.S.P. 2020291). The condensation products of acetaldehyde with  $\alpha$ -naphthylamine (Clayton Aniline Co., B.P. 316761) or with a mixture of  $\alpha$ - and  $\beta$ -naphthylamines (B.D.C., B.P. 280661) have found a considerable use for the same purpose. The condensation product of aldol and  $\alpha$ -naphthylamine has also been proposed as an "anti-ager" (Goodrich, U.S.P. 1855788; I.G., B.P. 333941). Thio- $\beta$ -naphthol is used as a plasticiser in the milling of unvulcanised rubber (Du Pont, B.P. 490292; I.C.I., B.P. 498302).

A somewhat closely allied problem is the *stabilisation of fuel oil*. Both phenyl- $\beta$ -naphthylamine and  $\alpha$ -naphthol have been proposed for this purpose (Gulf Oil Corp., U.S.P. 2048770; Gasoline Antioxidant Co., U.S.P. 2053466) as well as 1:5-dihydroxynaphthalene (Du Pont, U.S.P. 2053421). Naphthalene may also be used in the petroleum industry for de-waxing (Katz, Przemysl Chem. 1934, 18, 408). For retarding oxidation of *vegetable or animal oils* both phenyl- $\beta$ -naphthylamine and  $\alpha$ -naphthol have been proposed (Du Pont, U.S.P. 2041836; Gill Corp., U.S.P. 2036471). Olcott (J. Amer. Chem. Soc. 1934, 56, 2492) studied the prevention of autoxidation of lard by hydroxy-naphthalenes.

Tri- $\beta$ -naphthyl phosphate has been proposed as an addition to *high-pressure lubricants* (N. V.

de Bataafsche Pet. Maat., B.P. 424380) and tri- $\beta$ -naphthyl phosphite similarly to prevent corrosion of bearings (Socony Vac. Oil Co., U.S.P. 2058342).

An important use for alkyl-naphthalenesulphonic acids is as *wetting and emulsifying agents* (see under alkyl-naphthalenes, pp. 401d, 402c). The condensation product of naphthalenesulphonic acid and formaldehyde also finds application as a leather *tanning agent* (Badische, G.P. 292531). The formaldehyde condensation products of naphthol- and naphthylamine-sulphonic acids have also been proposed as tanning agents (Deutsch. Kolonial Gerb- u. Farbstoff-Ges., G.P. 293041; 293640).

As *insecticide*, crude naphthalene is a time-honoured soil dressing for control of wireworms. It is also used in control of millipedes (Orchard, Ann. Report of Expt. Res. Sta., Cheshunt, 1933, 19, 76) and in greenhouse fumigation (Speyer, *ibid.* 1935, 21, 68).  $\alpha$ -Naphthylamine and  $\alpha$ -naphthol have been used for control of codling moth larvae (Steiner and Marshall, J. Econ. Entomol. 1931, 24, 1146). Polychlorinated naphthalene ("*Halowax*," "*Seckay Wax*") has also been used as an ovicide against blow-fly (Breakey and Miller, *ibid.* 1935, 28, 358) and patented as a protection for wool and textile fabrics against insect attack (Gracser-Monsanto, B.P. 233993).

A recent important development in horticulture is the use as *plant growth stimulant* of  $\alpha$ -naphthylacetic acid which vies with indolylacetic acid in potency (Zimmermann and Wilcoxon, Contr. Boyce Thompson Inst. 1935, 7, 209).

In the field of *medicinal products*  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid is used for the preparation of the urea of *m*-aminobenzoyl-*m*-aminomethylbenzoyl-1-naphthylamine-4:6:8-trisulphonate known as Bayer-205 and "*Antrypol*," an effective trypanocide (Poulenc Freres, B.P. 224849; cf. Fournieu *et al.*, Compt. rend. 1924, 178, 675).  $\beta$ -Naphthylaminetri-sulphonates have been used to precipitate the active principles of diphtheria toxin and antitoxin (Goldie, Compt. rend. Soc. Biol. 1935, 119, 402; 1937, 124, 550, 1215).  $\beta$ -Naphthyl benzoate and salicylate are used medicinally (Schwyzer, Pharm. Ztg. 1931, 76, 186). A study of local anaesthetics in the naphthalene series was made by Blicke, Parke, and Jennor (J. Amer. Chem. Soc. 1940, 62, 3316), of sympathomimetics by Rajagopalan (J. Indian Chem. Soc. 1940, 17, 567). [ $\alpha$ ]Naphthaquinone derivatives have antihæmorrhagic (Vitamin-K) activity (*v.* alkyl-naphthalenes, p. 399a and Vol. VII, 87a).

#### REACTIONS OF NAPHTHALENE.

*Reduction*.—Being an unsaturated aromatic hydrocarbon, naphthalene under the action of reducing agents can be hydrogenated, forming di-, tetra-, hexa-, octa-, and deca-hydrides. The reduction of naphthalene will be fully discussed under a separate heading devoted to hydrogenated naphthalenes. The tetra- and deca-hydrides, known respectively as totalin and decalin, are of considerable technical importance.

*Oxidation*.—Oxidation of naphthalene, and of its derivatives, may give two types of product,

according to whether the naphthalene skeleton remains intact or whether fission of one ring occurs. The most usual product of the first type obtained by direct oxidation is [ $\alpha$ ]naphthaquinone; of the second type, phthalic acid or its anhydride. Hydroxyl derivatives (the naphthols) are not obtained by oxidation of naphthalene. When [ $\alpha$ ]naphthaquinone is produced it is accompanied by phthalic acid and other products, as in oxidation by chromic acid in acetic acid solution (Groves, J.C.S. 1873, 26, 209; F. Beilstein and A. Kurbatow, Annalen, 1880, 202, 215); by oxidation with ceric sulphate in sulphuric acid solution (Höchst, G.P. 158609); and by electrolytic oxidation in presence of cerous salts (Höchst, B.P. 19178, 1902). In the last-mentioned process, 20% sulphuric acid containing cerous sulphate forms the electrolyte, the temperature being kept at 40–60°; eventually all the naphthaquinone can be oxidised, the product being phthalic acid. The anodic oxidation of naphthalene has also been studied by E. G. White and A. Lowy, who constructed an anode consisting of a mixture of 60% of naphthalene and 40% of carbon pressed on platinum gauze, and obtained at 25° a 25% yield of [ $\alpha$ ]naphthaquinone with some phthalic acid (Trans. Electrochem. Soc. 1932, 62, 107).

When heated with neutral aqueous permanganate or manganate solution, naphthalene can be oxidised to an intermediate product, phthalonic acid,  $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})\text{CO}\cdot\text{CO}_2\text{H}$ . J. Tscherniac obtained 10 parts of phthalonic acid, 1.4 parts of phthalic acid, and 3.5 parts of unchanged naphthalene from 12 parts of naphthalene (G.P. 79693; 86914; see also Procházka, Ber. 1897, 30, 3109; Gräbe and Trümper, *ibid.* 1898, 31, 369; Daly, J. Physical Chem. 1907, 11, 93). Other powerful oxidants such as nitric acid ( $\rho$  1.15) at 130°, and chromic-sulphuric acid, give phthalic acid.

The discovery in 1896 by the Badische Co. that naphthalene could be oxidised in high yield to phthalic acid by heating with 15 parts of sulphuric acid (monohydrate) and 0.5 parts of mercuric sulphate at 200–300° (G.P. 91202; B.P. 18221, 1896) was of great technical importance as it provided a cheap process for the manufacture of phthalic anhydride; this process has since been superseded by one based on the vapour-phase oxidation of naphthalene to phthalic anhydride by air in presence of vanadium pentoxide at 350–500°, discovered at about the same time by the Seldon Co. and Gibbs (B.P. 119518) and by A. Wohl (B.P. 145071). Large numbers of patents have since been taken out covering the control and improvement of this process (*v.* PHthalic ANHYDRIDE). Vanadyl chloride can be used in the stream of naphthalene and air, in place of the solid vanadium pentoxide catalyst (B.D.C., A. G. Green, and Porter, B.P. 164785). S. J. Green, who isolated some [ $\alpha$ ]naphthaquinone from the oxidation product using the latter catalyst, considered it to be probably an intermediate product (J.S.C.I. 1932, 51, 159r) and showed that totalin gave a similar yield of phthalic anhydride. Recently A. Pongratz and co-workers have studied the oxidation of substituted naphthalene derivatives by air over a vanadium pentoxide catalyst



whilst  $\alpha$ -chloronaphthalene gives mainly phthalic anhydride and very little 3-chlorophthalic anhydride, the ratio being 97:3,  $\beta$ -chloronaphthalene gives phthalic and 4-chlorophthalic anhydride in nearly equal amounts (53:47). The results, however, may be complicated through the occurrence of dehalogenation, for it is found that 1:5-dichloronaphthalene yields a product containing 80% of 3-chlorophthalic and 20% of phthalic anhydride (Angew. Chem. 1941, 54, 22).

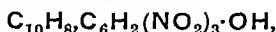
That  $\alpha$ -nitronaphthalene by vapour phase catalytic oxidation gives a high yield of phthalimide was discovered and patented by B.D.C., A. G. Green, and S. J. Green (B.P. 183044). Experimental work on the subject was published by S. J. Green (J.S.C.I. 1932, 51, 147r), and Pongratz (*l.c.*) found that the solid product contained 80% of phthalimide and 10% of phthalic anhydride. By oxidising  $\alpha$ -naphthylamine and  $\alpha$ -cyanonaphthalene the same author obtained much phthalimide, whilst  $\beta$ -naphthylamine gave more anhydride than imide.

According to G. Walter, chlorosulphonic acid at 180° converts naphthalene into tetrachlorophthalic anhydride (Monatsh. 1934, 64, 287). J. Boesken and G. Slooff have observed the slow conversion of naphthalene into 2-carboxyallo-cinnamic acid by peracetic acid in acetic acid (Rec. trav. chim. 1930, 49, 100).

The formation of  $\beta\beta$ -dinaphthyl by passing naphthalene through a red-hot iron tube has been observed (Ferko, Ber. 1887, 20, 662).

*Halogenation, Nitration, Sulphonation* (see pp. 275a, 288a, 270d, 280a).

*Molecular Compounds.*—Naphthalene, like many aromatic hydrocarbons including alkyl-naphthalenes, forms crystalline additive compounds with many polynitro-compounds, *e.g.*, with trinitro-derivatives of benzene (Hepp, Annalen, 1882, 215, 380), toluene (Hepp, *l.c.*), aniline (Liebermann and Palm, Ber. 1875, 8, 377), phenol (Henriques, Annalen, 1882, 215, 332) and cresol (Noelting, Ber. 1882, 15, 1862; 1884, 17, 271). The *picrate*,

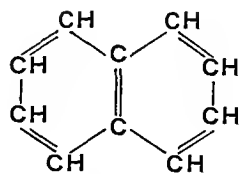


golden yellow needles, m.p. 149–151.5° (various authors), is soluble without decomposition in alcohol, ether, and benzene; the *styphnate*, m.p. 163.5°, has been studied by Jefremow (J. Russ. Phys. Chem. Soc. 1919, 51, 353; Chem. Zentr. 1923, III, 770). The solubility of naphthalene picrate in benzene and tetralin has been studied by L. Piatti (Z. angew. Chem. 1931, 44, 519). There is evidence that dinitro-compounds such as *m*-dinitrobenzene (E. L. Skau, J. Amer. Chem. Soc. 1930, 52, 945) and 1-bromo-2:4-dinitrobenzene (Buehler, Hisey, and Wood, *ibid.* 1930, 52, 1939) also form compounds with naphthalene.

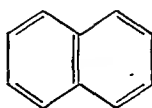
#### CHEMICAL CONSTITUTION.

The molecular formula of naphthalene is  $\text{C}_{10}\text{H}_8$ . The accepted structure, first proposed by Erlenmeyer (Annalen, 1865, 137, 346, footnote), and made probable on the basis of experimental evidence by Graebe (*ibid.* 1869, 149, 22) consists of two six-membered rings of carbon atoms having two adjacent atoms in common, a hydrogen atom being combined

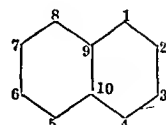
with each of the other eight carbon atoms, as in (I).



I.



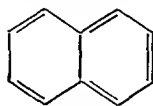
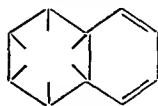
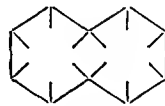
II.



III.

The abbreviated formulae (II) and (III) are commonly used. The carbon atoms are numbered as shown in III. Positions 1, 4, 5, and 8 are known as  $\alpha$ -positions, and 2, 3, 6, and 7 as  $\beta$ -positions. Positions 1 and 8 (or 4 and 5) are together referred to as *peri*-positions.

Whilst the Graebe-Erlenmeyer formula is completely satisfactory in its representation of the manner in which, in the naphthalene molecule, carbon is combined with carbon and carbon with hydrogen, the same degree of certainty has not been achieved regarding the disposition of the fourth valency of each carbon atom. The questions most discussed have been whether the naphthalene molecule is symmetrical with respect to the arrangement of the double bonds; whether either or both rings is better represented by a "centric" formula; and whether the double bonds, if present, occupy fixed positions. These questions have generally been considered in the light of the chemical behaviour of naphthalene and its derivatives, and will be referred to in the discussion on substitution in the naphthalene nucleus. Alternative structures which have been proposed for naphthalene to account for some of its properties are shown in (IV), (V), and (VI).

IV.  
Harries.V.  
Willstätter and  
Waser.VI.  
Bamberger.

#### Substitution in Naphthalene and Its Derivatives.

The symmetrical formula (I) shows two and only two kinds of hydrogen atoms, attached to  $\alpha$ - and  $\beta$ -carbon atoms respectively. Consequently, replacement of one hydrogen atom by any substituent should give rise to two different compounds with the substituent in the  $\alpha$ - and



the  $\beta$ -position respectively. In agreement with this prediction, two and only two mono-substituted naphthalenes containing the same substituent are known. It can also be predicted that, when the substituents are alike, there can be 10 di-, 14 tri-, and 22-tetra-substituted derivatives; with two different substituents there can be 14 isomers; with three substituents, two being alike, 42, and with three different substituents, 84. In a few instances, all the different isomers have been prepared. Notably, Armstrong and Wynne (Proc. C.S. 1890, 6, 77; 1895, 11, 84) completed the preparation of all the di- and tri-chloronaphthalenes, and established their orientation. (For a summary of their work, see H. E. Armstrong Obituary Notice, E. H. Rodd, J.C.S. 1910, 1422). Since, by a series of chemical reactions, many groups can be replaced by chlorine, the chloronaphthalenes can be used as reference compounds to fix the orientation of other naphthalene derivatives.

The course of substitution in naphthalene and its derivatives can be summarised as follows:

Substitution takes place far more readily in the  $\alpha$ - than in the  $\beta$ -position. Thus when naphthalene is halogenated or nitrated, the first product is predominantly the  $\alpha$ -nitro- or  $\alpha$ -halogeno-compound. Although long suspected, only recently has it been established that  $\alpha$ -nitronaphthalene is accompanied by a small proportion of the  $\beta$ -compound, and that  $\alpha$ -chloronaphthalene, as normally prepared, contains 5-10% of the  $\beta$ -isomer (E. C. Britton and W. R. Reed, U.S.P. 1917822). Sulphonation of naphthalene at moderate temperatures gives mainly the  $\alpha$ -sulphonic acid, which changes into  $\beta$ -sulphonic acid when heated at higher temperatures. This subject is discussed more fully under "Sulphonation of Naphthalene" (p. 270*d*), but it appears to be definitely established that in the initial reaction some  $\beta$ -sulphonic acid is always formed. Similarly, in the Friedel-Crafts reaction, acylation, e.g., acetylation and benzylation, of naphthalene gives a mixture of  $\alpha$ - and  $\beta$ -compounds; indeed, acetylation in nitrobenzene even at a low temperature gives predominantly  $\beta$ -naphthyl methyl ketone.

The formation of disubstituted and trisubstituted derivatives is much more complicated for naphthalene than for benzene. In the case of benzene the position taken up by a second entering substituent depends almost entirely on the nature of the substituent already present. In the case of naphthalene, it is not only governed by this factor, but in addition it depends on the position,  $\alpha$  or  $\beta$ , occupied by the group already present, and to a very important extent on the identity of the entering group and on the conditions prevailing at the time of the attack. Other factors, such as the greater susceptibility of naphthalene to substitution in the  $\alpha$ - than in the  $\beta$ -position come into play. It is, therefore, not possible to formulate definite rules, but the following generalisations can be made:

or 1-position direct entering groups into the 4- and 2-positions.

2. The same groups in the  $\beta$ - or 2-position in naphthalene direct entering groups into the 1-position or into the unsubstituted nucleus. The 3-position is only rarely attacked.
3. When a group which, in benzene, would cause substitution in the  $m$ -position ( $\text{NO}_2$ ,  $\text{SO}_3\text{H}$ , etc.) is present in either an  $\alpha$ - or  $\beta$ -position in naphthalene, a second group will enter the unsubstituted nucleus.

It must be understood that these generalisations are by no means binding. For instance, acyl derivatives of 1-naphthylamine when nitrated give, besides 4-nitro-, also 5- and 8-nitro-derivatives. Again, diazonium compounds attack  $\beta$ -naphthol and  $\beta$ -naphthylamine only in the 1-position, hetero-nuclear compounds never being formed, a fact of great importance in dye-stuff chemistry. Nitration and sulphonation may follow different courses. For instance, further nitration of 1-nitronaphthalene gives both 1:5- and 1:8-dinitronaphthalene, and nitration of naphthalene- $\alpha$ -sulphonic acid gives both 6- and 8-nitro-derivatives. But further sulphonation of naphthalene- $\alpha$ -sulphonic acid gives mainly the 1:5- and no 1:8-disulphonic acid. This is an example of the operation of the "law" first enunciated by Armstrong and Wynne that in the sulphonation of naphthalene derivatives, products are not obtained in which two sulphonic groups are present in contiguous  $\alpha\beta$ - or  $\beta\beta$ -positions, or 1:4- or 1:8-positions. Yet even this "law" has its exceptions, for when the sulphonating agent was 40-70% anhydrosulphuric acid it was found by O. Dressel and R. Kotho (Ber. 1894, 27, 1193) that by sulphonating 2-naphthol-7-sulphonic acid, 2-naphthol-1:3:6:7-tetrasulphonic acid is obtained, and by sulphonating 2-naphthylamine-3:7-disulphonic acid, 2-naphthylamine-1:3:6:7-tetrasulphonic acid is formed, in each of which two sulphonic groups are contiguous.

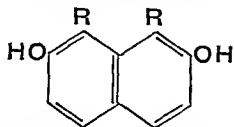
The most striking difference between naphthalene and benzene derivatives is afforded by the fact that whereas in phenol and aniline there is no distinction between the two *ortho*-positions, in 2-naphthol and 2-naphthylamine only the 1-position shows the properties of an *ortho*-position, the 3-position being singularly inert. Thus  $\beta$ -naphthol and  $\beta$ -naphthylamine couple with diazo-compounds only in the 1-position; when it is brominated,  $\beta$ -naphthol is substituted first in position 1, followed by position 6, then 4 and 3 (Franzen and Stauble, J. pr. Chem. 1921, [ii], 103, 352; Fries and Schimmelschmidt, Annalen, 1930, 484, 245); nitrosation of  $\beta$ -naphthol occurs only in position 1. So strong is the tendency of  $\beta$ -naphthol to couple in position 1 that if a sulphonic or chlorine group is present in that position it will be displaced by the arylazo-group. Such facts as these have led many chemists to the conclusion that in naphthalene compounds there is a fixed double bond between positions 1 and 2, and a single bond between positions 2 and 3. This conclusion has been strongly supported by, amongst many

1. Groups such as  $\text{CH}_3$ ,  $\text{Cl}$ ,  $\text{OH}$ ,  $\text{NHAc}$ , which in benzene are  $p$ - and  $o$ -directing, when present in naphthalene in the  $\alpha$ -

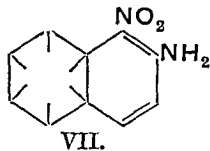
others, von Weinberg (Ber. 1921, 54 [B], 2168), K. Fries (Annalen, 1927, 454, 121; 1935, 516, 249), and Fieser and Lothrop (J. Amer. Chem. Soc. 1935, 57, 1459). Fries considers that "naphthoid" compounds are distinguished by the non-equivalence of *ortho*-positions and the presence of a double bond between the two carbon atoms common to both rings. This double bond fixes the Erlenmeyer structure, and is therefore responsible for the fact that naphthalene is relatively more unsaturated than benzene, and is reducible by sodium and alcohol, for example. It must be assumed that, at higher temperatures, the fixity of the double bond is released, allowing the possibility of attack in the 3-position, with formation, for example, of 2:3-hydroxynaphthoic acid from the 2:1-compound, and of  $\beta$ -naphthol-3:6-disulphonic acid in the sulphonation of  $\beta$ -naphthol. 1-Nitro- $\beta$ -naphthylamine is mercurated by mercuric acetate in the 3-position (Hodgson and Elliott, J.C.S. 1939, 345).

The fact that all attempts to obtain 2:3-naphthaquinone by oxidising 2:3-dihydroxynaphthalene, have failed, is also taken as evidence in favour of the Erlenmeyer formula, since, if the latter had a double bond in the 2:3-position, oxidation to a quinone might be expected. Another piece of evidence differentiating the 2:1- from the 2:3-positions is the fact that the bromine in 1-bromo-2-naphthylamine is readily removed by boiling with aqueous stannous chloride whilst that in 3-bromo-2-naphthylamine is unaffected; 1:3-dibromo-2-naphthylamine loses only the bromine in position 1 (R. B. Sandin and T. H. Evans, *ibid.* 1939, 61, 2916).

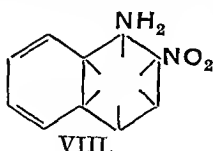
Experimental support for the symmetrical character of the naphthalene ring system has been provided by Fieser and Lothrop (*l.c.*) who prepared derivatives of 2:7-dihydroxynaphthalene containing alkyl groups, R, in both 1 and 8 positions. Such compounds failed to couple with diazo-compounds, positions 3 and 6 being equally inactive. Similar inactivity was shown by 2:6-dihydroxy-1:5-dialkylnaphthalenes.



The alternative formulæ (IV), (V), and (VI) have received little support in recent literature. F. Mayer and A. Bansa (Ber. 1921, 54 [B], 16) tried to account for the fact that 1-nitro-2-naphthylamine is a stronger base than 2-nitro-1-naphthylamine by giving them respectively the



VII.



VIII.

structures (VII) and (VIII). It has also been suggested that the yellow colour of 2:3-hydroxynaphthoic acid and its ester and anilide are due to a double bond between the 2- and 3-positions,

giving the Harries structure (Lesser, Kranepuhl, and Gad, *ibid.* 1925, 58 [B], 2109), and W. Baker and G. N. Carruthers assumed a similar departure from the Erlenmeyer structure in 3-acetyl-2-naphthol, which is also yellow in colour (J.C.S. 1937, 479). J. Obermiller has drawn attention to the special relation apparently existing between the 2- and 6-positions in naphthalene (J. pr. Chem. 1930, [ii], 126, 257). V. N. Ufimzev has suggested that in monosubstituted naphthalenes the unsymmetrical (Harries) structure is assumed, the unsubstituted ring becoming benzenoid, and substitution taking place in this ring accordingly. The argument, however, is not satisfactory (Ber. 1936, 69 [B], 2188; J. Gen. Chem. Russ. 1935, 5, 653).

During recent years the problem of the structure of naphthalene has attracted the efforts of physicists and mathematicians. J. M. Robertson, from X-ray crystallographic data, concludes that the molecule has the form of two fused plane hexagons, the C—C distances being 1.41 Å. (Proc. Roy. Soc. 1933, A, 142, 674). Several workers have applied wave-mechanical principles and the theory of resonance to the study of the subject. The true structure of naphthalene may be something between the Erlenmeyer and Harries representations, and the balance of opinion seems to be that the former contributes more to the structure than the latter; in other words, the 1:2-position has more double-bond character than the 2:3-position (J. Sherman, J. Chem. Physics, 1934, 2, 488; L. Pauling *et al.*, J. Amer. Chem. Soc. 1935, 57, 2708; S. Rangaswami and T. R. Seshadri, Proc. Indian Acad. Sci. 1941, 14A, 547). Physical properties which have been studied recently in relation to the structure of naphthalene and its derivatives are *absorption spectra* (F. Krollpfeiffer, Annalen, 1923, 430, 181; Henri and de László, Compt. rend. 1924, 178, 1004; Proc. Roy. Soc. 1924, A, 105, 662; de László, Z. physikal. Chem. 1925, 118, 369; Proc. Roy. Soc. 1926, A, 111, 355; K. Lauer, Ber. 1936, 69 [B], 986); *Raman spectrum* (K. W. F. Kohlrausch, *ibid.* 1935, 68 [B], 893; G. B. Bonino, Gazzetta, 1936, 66, 827); *molecular refraction* (K. von Auwers and A. Frühling, Annalen, 1920, 422, 192; K. Fries and H. Bestian, Ber. 1936, 69 [B], 715); and *dipole moments* (Parks, Z. physikal. Chem. 1930, B, 10, 264; Williams and Fogelberg, J. Amer. Chem. Soc. 1931, 53, 2096; Nakata, Ber. 1931, 64 [B], 2059). The influence of constitution on the fluorescence of salts of naphthalene-, naphthylamine- and naphthol-sulphonic acids has been studied by Allen, Franklin, and McDonald (J. Franklin Inst. 1933, 215, 705).

**Sulphonation.**—The process of sulphonation is used to obtain many important dyestuff intermediates, being applied to naphthalene itself and to its derivatives, particularly  $\beta$ -naphthol and the naphthylamines. The process is in no case simple, and much study has been given to the subject both in industrial and academic laboratories. The process is frequently complicated by the occurrence of so-called isomerisation, that is, the conversion of an initially formed sulphonic acid into a different one as the reaction proceeds, and as this phenomenon has

been little studied except in the naphthalene series it merits special description.

*Isomeric Change of Naphthalenesulphonic Acids.*—When naphthalene is sulphonated at a low temperature the  $\alpha$ -sulphonic acid is formed, but at higher temperatures, or when the  $\alpha$ -sulphonic acid is heated with sulphuric acid, the  $\beta$ -sulphonic acid is formed. This apparent isomerisation of  $\alpha$ -sulphonic into  $\beta$ -sulphonic derivatives at elevated temperatures is of frequent occurrence in naphthalene chemistry. Several investigators, in particular P. C. J. Euwens (Rec. trav. chim. 1909; 28, 298), I. S. Yoffe (Anilinokras. Prom. 1933, 3, 296; A. 1934, 178), and R. Lantz (Bull. Soc. chim. 1935, [v], 2, 2092) have studied the phenomenon in the case of naphthalene itself, and as a result of their work it is fairly certain that the change of  $\alpha$ -into  $\beta$ -acid is not due to a true intramolecular isomeric change, but comes about through hydrolysis of the  $\alpha$ -sulphonic and re-sulphonation to a more stable  $\beta$ -sulphonic acid, as suggested first by Noelting (Ber. 1875, 8, 1095). Nevertheless, the work of Yoffe and Lantz, and also that of Fierz and Weissenbach (Helv. Chim. Acta, 1920, 3, 312) shows that even at 0° pure  $\alpha$ -sulphonic acid is not formed but is always accompanied by some  $\beta$ -sulphonic; at 0° using monohydrate Fierz and Weissenbach found 2% of  $\beta$ -acid in the product.

Euwens studied the reaction between naphthalene and monohydrate\* in molecular proportion at temperatures between 80° and 173° during 8 hours in each case. Between 80° and 161° the amount of unchanged naphthalene diminished from 27.0% to 6.0% and the proportion of  $\alpha$ -acid in the product fell from 96.4% to 18.4%. (The ratio of  $\alpha$ - to  $\beta$ -acid was determined from the solubility of the lead salts.) He found that at the high temperatures of 158° and 173° he could arrive at a mixture of the same composition either by heating naphthalene- $\beta$ -sulphonic acid with sulphuric acid or by starting with naphthalene, thereby proving the reversibility of both  $\alpha$ - and  $\beta$ -sulphonations. At 129°, however, starting with naphthalene or with  $\alpha$ -sulphonic acid, after 8 hours the resulting sulphonic acids contained 44% of  $\alpha$ -acid, whereas starting with pure  $\beta$ -sulphonic acid the product contained only 17.7% of  $\alpha$ -acid; that is to say, a state of equilibrium was not reached. This anomaly was explained by Yoffe, who found that at lower temperatures, e.g., 100°, 8 hours is wholly insufficient time to establish equilibrium. Using the same conditions as Euwens he found:

After 8 hours at 100°	81.0% of $\alpha$ -sulphonic acid.
" 100 "	41.1% " "
" 300 " "	29.3% " "

Lantz, in designing his experiments, realised that, when using naphthalene and monohydrate in molecular proportion, the strength of the acid rapidly falls as sulphonation proceeds due to formation of water and disappearance of acid. He therefore studied the rate of sul-

phonation of naphthalene using a large excess of acid (2 c.c. of acid to 0.1 g. of naphthalene) at different temperatures and acid concentrations. The following figures are from his paper:

Temperature.	Strength $H_2SO_4$ %.	Time.	Per cent. sulphonated.
180°	70.3	2½ hours	99.4
180°	57.7	3 "	2.5
180°	57.7	39 "	10.4
180°	51.4		No sulphonation
60°	94.4	½ "	96.9
60°	88.3	1 "	39.0

The effect of acid concentration on speed of sulphonation is very marked. Similarly, the rate of desulphonation increases with the strength of acid. At 140° it was found, using acids of 45.1 and 51.4% strength, that the  $\alpha$ -acid was desulphonated approximately 50 times as fast as the  $\beta$ -acid. An important experiment was made, in which sodium naphthalene- $\alpha$ -sulphonate was heated at 140° with (a) 64.2% sulphuric acid, i.e., above sulphonating strength and (b) 45.9% acid, below sulphonating strength. In (a) after 4 hours the sulphonic acid contained only 18.5% of  $\alpha$ -isomer, rapid conversion to the  $\beta$ -form having occurred; in (b) no conversion took place. Thus conversion accompanies hydrolysis and appears to be dependent thereon. Another important finding resulted from an experiment in which sulphonation was carried out with acids of strengths 81.7, 85.1, and 94.4% for as short a time as possible at 20° and 60° to give a reasonable amount of sulphonic acid for analysis. It was found that the proportions of  $\alpha$ - and  $\beta$ -isomer were independent both of temperature and acid strength, the mean composition of the initially formed sulphonic acid being 89–90% of  $\alpha$  and 10–11% of  $\beta$ . The proportion of  $\beta$ -acid increases, with time, more rapidly the stronger the acid.

The experimental results are therefore in agreement with the conclusions arrived at by both Lantz and Yoffe, that the course of sulphonation is determined by (a) the ratio of the velocities of formation of  $\alpha$ - and  $\beta$ -acids; (b) the ratio of the velocities of their hydrolytic desulphonation. It follows from the law of mass action that at equilibrium the concentrations,  $C_\alpha$  and  $C_\beta$ , of the two acids are given by the equation:

$$\frac{C_\alpha}{C_\beta} = \frac{\text{Velocity coeff. of formation of } \alpha}{\text{Velocity coeff. of formation of } \beta} \div \frac{\text{Velocity coeff. of hydrolysis of } \alpha}{\text{Velocity coeff. of hydrolysis of } \beta}$$

The ratios of the velocity coefficients are not known accurately; Lantz gives provisionally 10:1 for formation and 50:1 for hydrolysis, giving  $C_\alpha/C_\beta = \frac{1}{5}$  or 20% of  $\alpha$ -acid at equilibrium. It is probable, however, that this figure is too high; O. N. Witt, in his description of the process on which the technical manufacture of the  $\beta$ -sulphonic acid is based, gives a ratio of  $\beta$ : $\alpha$

\* In this article "sulphuric acid," when not otherwise distinguished, is ordinary concentrated (ca. 98%) sulphuric acid of  $\rho$  1.845; "monohydrate" is 100% sulphuric acid; "anhydro-acid" is fuming sulphuric acid or "oleum" containing dissolved sulphur trioxide, the proportion of which is given when known.

=85:15, after only 20 minutes heating at 160° (Ber. 1915, 48, 743).

Sulphonic groups can migrate from one  $\alpha$ -position to another more stable  $\alpha$ -position, as was shown by A. G. Green and K. H. Vakil in their study of the mono-sulphonation of  $\beta$ -naphthylamine. The two chief products of sulphonation with concentrated sulphuric acid at temperatures up to 120° are the 8- and 5-sulphonic acids, about 44% of the former and 55% of the latter. The 8-sulphonic acid when heated with concentrated sulphuric acid is gradually changed into a mixture of the 5- and 8-sulphonic acids, the authors attributing the change to hydrolysis followed by resulphonation. They could not, however, bring about the reverse change of the 5- into the 8-sulphonic acid. At temperatures above 120° the 6- and 7-sulphonic acids make their appearance in increasing amount (J.C.S. 1918, 113, 35).

Erdmann, at an earlier date (Annalen, 1893, 275, 192), had explained the phenomena observed in the sulphonation of  $\alpha$ -naphthylamine in a similar way. When  $\alpha$ -naphthylamine is heated at 130° with 95-96% sulphuric acid, the 4-sulphonic acid is formed in major amount, with some 5- and a trace of 6-sulphonic acid. As heating is prolonged, however, free naphthylamine appears in increasing amount, with some 4:7-disulphonic acid, whilst the 4-sulphonic acid is gradually replaced, first by the 5- and then by the 6-sulphonic acid. Here, apparently, speed of formation and of hydrolysis are in the order 4->5->6-sulphonic acid, with the result that, given sufficient time, the last predominates in the product.

Further information on the phenomena of sulphonation will be given when the sulphonation products of naphthalene and its important derivatives are described.

**Coupling with Diazo-compounds.**—One of the most important applications of naphthalene derivatives is their use as components of azo-dyestuffs. For this purpose they can function in two ways, either as diazo-components, in which case the molecule must contain a diazotisable amino-group, or as coupling components, when either an amino- or a hydroxyl group must be present to facilitate and direct combination with a diazo-compound whereby formation of an azo-compound is effected. As coupling components there are the naphthols and naphthylamines, their mono- and di- and tri-sulphonic acids, and a number of amino-naphthols and sulphonic acids derived from these.

The sulphonic acids of naphthalene derivatives employed in dyestuff manufacture have acquired trivial names which are frequently used in place of their chemical names. The most important of these are as follows:

Chemical Name.	Trivial Name.
1-Naphthylamine-4-sulphonic acid.	Naphthionic Acid.
1-Naphthylamine-5-sulphonic acid.	Laurent Acid.
1-Naphthylamine-6-sulphonic acid.	Cleve Acid 1:6.
1-Naphthylamine-7-sulphonic acid.	Cleve Acid 1:7.
1-Naphthylamine-8-sulphonic acid.	Peri-Acid.

2-Naphthylamine-1-sulphonic acid.	Tobias Acid.
2-Naphthylamine-6-sulphonic acid.	Brönnner Acid.
2-Naphthylamine-7-sulphonic acid.	Amino-F-Acid.
2-Naphthylamine-8-sulphonic acid.	Badische Acid.
1-Naphthylamine-3:8-disulphonic acid.	e-Acid.
2-Naphthylamine-3:6-disulphonic acid.	Amino-R-Acid.
2-Naphthylamine-6:8-disulphonic acid.	Amino-G-Acid.
1-Naphthol-4-sulphonic acid.	Neville and Winther Acid.
1-Naphthol-5-sulphonic acid.	Oxy-L-Acid.
2-Naphthol-1-sulphonic acid.	Oxy-Tobias Acid (Armstrong Acid).
2-Naphthol-6-sulphonic acid.	Schäffer Acid.
2-Naphthol-7-sulphonic acid.	F-Acid.
2-Naphthol-8-sulphonic acid.	Crocein Acid.
1-Naphthol-3:6-disulphonic acid.	Violet Acid.
2-Naphthol-3:6-disulphonic acid.	R-Acid.
2-Naphthol-6:8-disulphonic acid.	G-Acid.
1-Amino-5-naphthol-7-sulphonic acid.	M-Acid.
1-Amino-8-naphthol-4-sulphonic acid.	S-Acid.
2-Amino-5-naphthol-7-sulphonic acid.	J-Acid.
2-Amino-8-naphthol-6-sulphonic acid.	$\gamma$ -Acid.
1-Amino-8-naphthol-2:4-disulphonic acid.	2S-Acid, Chicago Acid.
1-Amino-8-naphthol-3:6-disulphonic acid.	H-Acid.
1-Amino-8-naphthol-4:6-disulphonic acid.	K-Acid.
2-Amino-8-naphthol-3:6-disulphonic acid.	2R-Acid.
1:8-Dihydroxynaphthalene-3:6-disulphonic acid.	Chromotrope Acid.

In the  $\beta$ -series, the coupling rule is simple; the entering azo-group can only take up the 1-position, adjacent to the 2-hydroxyl or 2-amino-group. No heteronuclear coupling occurs, and the 3-position is never attacked. A substituent in the 8-position, such as the sulphonic group, renders coupling more difficult; thus crocein acid and G-acid couple less readily than Schäffer or R-acid. A negative group in the 4-position has a similar effect.

In  $\alpha$ -naphthylamine and  $\alpha$ -naphthol derivatives there are two coupling positions, the 2- and 4-positions, when these are unsubstituted. There is a greater tendency to couple in the 4-position than in the 2-position, but this tendency is profoundly modified by the presence of other substituents, particularly when these are in the 3- and 5-positions; further, the "strength" of the diazo-compound and the coupling conditions play their part. With  $\alpha$ -naphthols and  $\alpha$ -naphthylamines containing sulpho-groups in 3- or 5-positions the tendency is to couple in the 2-position. It was shown, however, by L. Gattermann and M. Liebermann (Annalen, 1912, 393, 198) that whilst diazotised sulphanilic acid couples with 1-naphthylamine-5-sulphonic acid in the 2-position, *p*-nitrodiazobenzene couples in both 2- and 4-positions, whilst dinitrodiazobenzene couples only in the 4-position. According to these authors, diazotised *p*-nitroaniline couples with  $\alpha$ -naphthylamine-3-sulphonic acid only in the 2-position but with  $\alpha$ -naphthylamine-5-sulphonic acid in both 2- and 4-positions, whereas with  $\alpha$ -naphthol-3-sulphonic acid, it couples in the 2- and 4-positions but with  $\alpha$ -naphthol-5-sulphonic acid only in the 4-position. The influence of coupling conditions is illus-

trated by some experiments quoted by Fierz-David (Angew. Chem. 1936, 49, 24) who found that the benzenediazonium salt of 1-naphthol-5-sulphonic acid when treated with mild alkali gives only the 2-benzeneazo-derivative, whilst with strong caustic soda it gives a mixture of 2- and 4-benzeneazo-compounds.  $\alpha$ -Naphthylamine itself couples to give some 2-substituted derivative, and it is claimed (Bayer, B.P. 238683, 1924) that by using  $\alpha$ -naphthylsulphamic acid,  $C_{10}H_7NHSO_3H$ , coupling with diazo-compounds exclusively in the 4-position can be obtained.

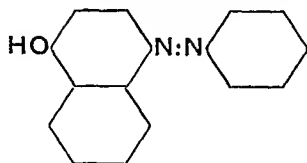
It is interesting to note that 1:5-dihydroxynaphthalene couples generally with only 1 mol. of a diazo-compound, the position attacked being 2 in strong alkali and 4 in mild alkali. With strong coupling components some 2:4-bisazo-compound can be obtained (O. Fischer and Bauer, J. pr. Chem. 1916, [ii], 94, 13; 1917, [ii], 95, 264) but coupling never takes place in both rings of the naphthalene molecule.

As a general rule, coupling directed by an amino-group is favoured in acid solution, and that directed by a hydroxyl group in alkaline solution. Although this is not an invariable rule, it governs the procedure adopted when aminonaphthols and their sulphonic acids have to be coupled with diazo-compounds. Most of the technically important aminonaphtholsulphonic acids including H-acid, S-acid, and J-acid, will couple in both rings, the first coupling being carried out in acid and the second in alkaline solution. However,  $\gamma$ -acid

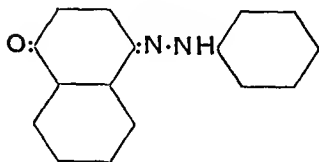


only couples satisfactorily once.

The benzeneazonaphthols are isomeric with the monophenylhydrazones of the corresponding naphthaquinones. Much work has been done on the relation between the two classes of compounds, and quite recently R. Kuhn and F. Bär have concluded that 4-benzeneazo- $\alpha$ -naphthol is indeed a tautomeric mixture of the two forms (I) and (II) in approximately equal amounts



I.



II

(Annalen, 1935, 516, 143). On the other hand, they conclude on chemical and spectroscopic evidence that 1-benzeneazo-2-naphthol and 2-benzeneazo-1-naphthol exist almost entirely in the quinonehydrazone forms. In this connection it is to be noted that benzeneazonaphthylamines in which the amino-group is adjacent to the azo-group are difficult to diazotise;

they are probably not true amino-compound but imines.

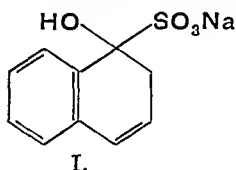
For further information on the behaviour of naphthalene derivatives in the preparation of azo-dyes, the reader is referred to the article on DYE STUFFS, Azo, Vol. IV, 190-239.

**The Bisulphite Reaction.**—A reaction deserving of special mention in any description of naphthalene chemistry is that by which naphthols can be converted into naphthylamines and *vice versa*, by means of bisulphite solutions. The reaction is of considerable importance technically for the preparation of  $\beta$ -naphthylamine and its derivatives, because  $\beta$ -nitronaphthalene cannot be prepared by nitration of naphthalene, and the  $\beta$ -amino is therefore not obtainable from this source.  $\beta$ -Naphthylamine can be obtained by heating  $\beta$ -naphthol with ammonia at  $150^\circ$ , but the reaction is slow and accompanied by by-products, including  $\beta\beta$ -dinaphthylamine, and a poor yield is obtained. When, however,  $\beta$ -naphthol is heated with excess of ammonia and ammonium sulphite solution, the reaction proceeds much more quickly and gives a high yield of  $\beta$ -naphthylamino (Badische, G.P. 117471; Bucherer, J. pr. Chem. 1904, [ii], 69, 88). Conversely it has been shown that naphthylamines can be converted into naphthols by heating with sodium bisulphite solutions at the boiling-point (Bayer, G.P. 109102). The clue to these results was supplied by H. T. Bucherer, who showed that in these reactions a highly soluble intermediate compound is formed which is stable towards acids but is decomposed by alkalis to give the naphthol, and by ammonia to give the naphthylamine, in almost quantitative yield. The intermediate compound, which he considered to be the naphthyl sulphite,  $C_{10}H_7O\cdot SO_2Na$ , can be obtained either from the naphthol or naphthylamino (G.P. 115335; 126136; B.P. 1387, 1900). If, instead of ammonia, a mono-, or di-alkylamino is used with bisulphite, a corresponding mono- or di-alkylnaphthylamine can be obtained (G.P. 121683; Bucherer, J. pr. Chem. 1904, [ii], 70, 345), whilst arylamines convert the  $\beta$ -naphthyl sulphites into  $\beta$ -naphthylarylamines (G.P. 122570). Both of these reactions are applied to the manufacture of derivatives of N-substituted naphthylamines.

When naphthylenediamines are heated with bisulphite solution only one amino-group is attacked; an interesting case is provided by 1:8-naphthylenediamine-4-sulphonic acid, which gives only 1:8-aminonaphthol-5-sulphonic acid. The isomeric 1:8-aminonaphthol-4-sulphonic acid can be obtained by the action of bisulphite on the acetone condensation product of the diamine-sulphonic acid (B.P. 16921, 1900; Bucherer, *l.c.*). The 1:8-aminonaphthol-4-sulphonic acid by further treatment with bisulphite gives 1:8'-dihydroxynaphthaleno-4-sulphonic acid, but the 1:8-aminonaphthol-5-sulphonic acid does not, since it forms a sulphurous ester with the hydroxyl group. The dihydroxynaphthalenes form only mono-sulphurous esters.

The bisulphite reaction finds many applications in the preparation of aminonaphtholsulphonic acids, and the limitations of the reaction are therefore important. Some of

these have been mentioned in the preceding paragraph; in addition, it does not take place with  $\alpha$ -derivatives in which a substituent, such as a sulphonic group, is present in the 2- or 3-position, or with  $\beta$ -derivatives in which there is a substituent in the 4-position. These limitations can be turned to advantage; for instance 2:8-dihydroxynaphthalene-6-sulphonic acid by the bisulphite reaction gives only 2-amino-8-naphthol-6-sulphonic acid ( $\gamma$ -acid), since the 8-hydroxy-group cannot be attacked. The same product can be obtained from *nigrotic acid*, 2:8-dihydroxynaphthalene-6-sulphonic-3-carboxylic acid (Bucherer and Seyde, J. pr. Chem. 1907, [ii], 75, 255). Bucherer's view that the intermediate product is a sulphite ester throws no light on the limitations of the reaction. An alternative is to regard it as a bisulphite additive compound of the ketonised form of the naphthol, as in (I), a formulation which accords



better with the mobility of the hydroxyl group and has some analytical support (Voroshnev, J. Russ. Phys. Chem. Soc. 1915, 47, 1669; König and Haller, J. pr. Chem. 1921, [ii], 101, 43; Friedländer, Ber. 1921, 54, [B] 620).

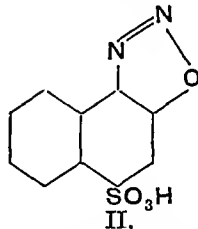
The discovery of the reaction between naphthylamines and bisulphite was apparently first made by Lepetit and recorded in a *pli cacheté* of 1896 (published in Bull. Soc. Ind. Mulhouse, 1903, 326; see Friedländer, l.c.), but the detailed study of the reaction was carried out by Bucherer, by whose name the reaction is known.

An interesting variant of the Bucherer reaction is the treatment of a naphthol with bisulphite and phenylhydrazine, when a naphthacarbazole is formed. When 2:3-hydroxynaphthoic acid is treated in this way the carboxyl group is eliminated during the reaction (Bucherer and Seyde, J. pr. Chem. 1908, [ii], 77, 403; G.P. 208960).

It may be mentioned here that when  $\alpha$ -nitronaphthalene is reduced with bisulphite, not only reduction but simultaneous sulphonation occurs with formation of naphthionic acid, and with excess of bisulphite,  $\alpha$ -naphthylamine-2:4-disulphonic acid (Höchst, G.P. 92082). In a similar way 1-nitroso- $\beta$ -naphthol gives 1-amino- $\beta$ -naphthol-4-sulphonic acid (q.v., p. 353c). It is interesting also to note that when 1:8-dinitronaphthalene-3:6-disulphonic acid is treated with bisulphite it is converted into 8-amino- $\alpha$ -naphthol-3:6-disulphonic acid, reduction being accompanied by replacement of nitro or amino- by hydroxyl (Bayer, G.P. 113944) the significance of which was noted by Bucherer (J. pr. Chem. 1904, [ii], 70, 349).

**Diazotisation of Naphthylamines; Diazo-oxides.**—Amines of the naphthalene series and their substituted derivatives can generally be diazotised normally with nitrous acid giving

diazonium compounds, many of which are used in the manufacture of azo-dyes (see DYESTUFFS, Azo, Vol. IV, 190–239). When the naphthylamine also contains a hydroxyl group abnormalities may arise. Should the hydroxyl group be in a position to promote coupling, precautions must be taken to prevent self-coupling when the amino-group is diazotised. When the hydroxyl-group is adjacent to the amino-group, as in 1:2- and 2:1-aminonaphthol and their sulphonic acids, nitrous acid in presence of free mineral acid brings about oxidation to [ $\beta$ ]naphthoquinone (Witt, Ber. 1888, 21, 3475; Böniger, *ibid.* 1894, 27, 24), but diazotisation can be effected by the action of sodium nitrite on the aminonaphtholsulphonic acid in absence of mineral acid, and the yield is improved when cupric salts are present (Geigy, B.P. 10235, 1904); other metal salts are also claimed to assist the diazotisation, e.g., zinc (Kalle, G.P. 175593; 195228; B.P. 23034, 1905), nickel (Kalle, G.P. 178621), manganese, cobalt, magnesium, mercuric (Kalle, G.P. 195322; 178936) and even salts of alkali and alkaline earth metals (Badische, B.P. 10323, 1906), but in practice copper salts are probably best. The diazo-compounds so formed readily pass by loss of water into stable diazo-oxides (formula of the well-known naphthalene-1-diazo-2-oxide-4-sulphonic acid, (II)), especially in the presence of mild alkali.



When there is present a "negative" group such as halogen, nitro- or sulphonic, adjacent to the amino-group, this group is readily removed from the diazo-compound with formation of a diazo-oxide. Thus Gaess and Ammelburg obtained 6-nitronaphthalene-2-diazo-1-oxide by diazotising 1:6-dinitro- $\beta$ -naphthylamine (Ber. 1894, 27, 2211), and Morgan and Evens obtained 4-nitronaphthalene-2-diazo-1-oxide when 1:4-dinitro- $\beta$ -naphthylamine was diazotised in strong sulphuric acid and the product diluted with water (J.C.S. 1919, 115, 1126). Meldola and Streatfield similarly obtained 4-bromonaphthalene-2-diazo-1-oxide from 1:4-dibromo- $\beta$ -naphthylamine (*ibid.* 1895, 67, 909). Examples of the replacement of a sulphonic acid group or a chloro-group adjacent to the diazo-group are recorded in several patents (Badische, B.P. 6615, 1902; 16995 and 27372, 1903; 4997 and 21638, 1904; Meister, B.P. 23993, 1902). Since the sulphonic group is eliminated in the form of sulphurous acid, it is advantageous to add an oxidising agent to convert this into sulphuric acid, to avoid subsequent complications when the diazo-compound is used for the preparation of dyestuffs. The diazo-oxides, when they contain sulphonic groups, couple with  $\beta$ -naphthol in alkaline media, but according to Morgan and Evens the nitronaphthalene diazo-oxides only



couple with very active phenols such as resorcinol in a strongly acid medium (*l.c.*). The stability of the diazo-oxides is shown by the fact that they can be chlorinated (Kalle, B.P. 20072 and 20073, 1911), brominated (Sandoz, B.P. 3508, 1911), nitrated (Geigy, B.P. 15418, 1904), and sulphenated (Kalle, G.P. 176618; 176620). The nitration of naphthalene-2-diazo-1-oxide-4-sulphonic acid is carried out technically, the product being the 6-nitro-derivative.

### CHLORONAPHTHALENES.

Naphthalene derivatives containing chlorine are of two kinds: (a) additive compounds such as naphthalene dichloride and tetrachloride, which are to be regarded as substitution products of di- and tetra-hydronaphthalene; (b) substitution products in which chlorine replaces one or more nuclear hydrogen atoms. The former type are formed by the action of chlorine on naphthalene in the cold, and on warming or in the presence of catalysts pass into the second type with loss of hydrogen chloride. The isomeric mono-, di-, and tri- and some of the tetra-chloronaphthalenes are all known, having been obtained by the following and other methods:

- (1) By the direct chlorination of naphthalene or chloronaphthalene, either in the liquid or gaseous phase, or in solution (Faust and Saame, *Annalen*, 1871, 160, 65; E. Fischer, *Ber.* 1878, 11, 735; Widman, *ibid.* 1882, 15, 2160; Armstrong and Wynne, *Proc. C.S.* 1890, 6, 85; Badische, G.P. 234912; Ferrero and Wunenburger, *Helv. Chim. Acta*, 1928, 11, 416; Ferrero and Fehlmann, *ibid.* 1929, 12, 583; Ferrero and Corbaz, *ibid.* 1930, 13, 1009).
- (2) From aminonaphthalenes by diazotisation and the Sandmeyer reaction (Friedländer and Szymanski, *Ber.* 1892, 25, 2081; Chattaway and Lewis, *J.C.S.* 1894, 65, 877).
- (3) By conversion of nitro-, amino-, and hydroxy-naphthalenes into chloronaphthalenesulphonic acids and subsequent hydrolysis (Cleve, *Ber.* 1892, 25, 2487).
- (4) By heating naphthalenesulphonyl chlorides or chloronaphthalenesulphonyl chlorides with phosphorus pentachloride or alene (Carius, *Annalen*, 1860, 114, 145; Armstrong, *Ber.* 1882, 15, 205; Armstrong and Wynne, *Proc. C.S.* 1895, 11, 80, 83; 1897, 13, 152).
- (5) By distillation of nitronaphthalene or nitronaphthalenesulphonyl chlorides with phosphorus pentachloride (De Koninck and Marquart, *Ber.* 1872, 5, 11; Erdmann and Süvern, *Annalen*, 1893, 275, 232, 252).

The direct chlorination of naphthalene has been studied by many workers, both in connection with the preparation of  $\alpha$ -chloronaphthalene and other individual compounds and for the production of more highly chlorinated compounds; the latter are mixtures, forming wax-like substances having valuable technical properties. In the first stages of chlorination

in the liquid phase the main product is  $\alpha$ -chloro- with a small proportion of  $\beta$ -chloro-naphthalene, and before all the naphthalene is chlorinated dichloronaphthalenes appear, mainly 1:4- and 1:5-, and trichloro-compounds. As chlorination proceeds, the setting point of the product rises to a maximum of 125–130° when some 60% of chlorine is present, thereafter falling.

The chlorination of naphthalene to give a hard pale-yellow wax was described by Payman and Gibson, I.C.I., who used a temperature of 140–160° with ferric chloride as a catalyst. The product contained up to 57% of chlorine (B.P. 291849) and a similar product was obtained by cold chlorination in carbon tetrachloride solution (B.P. 292056). The I.G. later claimed a similar product by chlorinating below 130° using antimony trichloride, phosphorus tri- or pentachloride, sulphur or iodine as catalyst (B.P. 324774), and a further I.C.I. improvement was to chlorinate in two stages, first at 85–110° to a monochloronaphthalene, then at 140–150° (B.P. 357743).

Alternative catalysts have been investigated by Selvemberger and Gordon (*J. Gen. Chem. Russ.* 1934, 4, 529) who found that the chlorination to octachloronaphthalene could be carried to completion without catalyst by starting without heating, and gradually raising the temperature to 200°. Chlorination time was considerably shortened by the addition of 0.3–1.0% of a metallic chloride (aluminium, ferric, gold, titanium, zirconium, antimony, or tellurium). Other chlorides were found to be less active or completely inactive. Iron powder, with or without iodine (Selvemberger and Gordon, *ibid.* 1932, 2, 921), alumina (Vorozhitsov and Travkin, *Russ. P.* 51042; *Amer. Chem. Abstr.* 1939, 33, 4604), and light (Consolidierte Alkaliwerke, G.P. 605780) have also been used. Iodine appears to favour the formation of mono-substituted products, whereas ferric chloride, alumina, etc., lead to the formation of polychloronaphthalenes. Kattscher and Minossenko (*Russ. P.* 41513) describe chlorination in the absence of catalyst.

When chlorination is carried out in cast-iron apparatus the crude product is a dark discoloured wax. Hydrogen chloride can be removed by blowing air or an inert gas through the molten mass (Rücker Chemical Foundation Inc., U.S.P. 1455509) and the wax can be purified by distillation under reduced pressure after neutralising with lime, caustic soda, etc. At 100–150 mm. pressure, mono- and dichloro-naphthalenes distil between 140–180°; higher fractions are collected at 200–225° and 225–250° (Halowax Corp., B.P. 343878).

Chlorination in the vapour phase occurs either with or without a catalyst at temperatures of 250–400°, with maximum yield of 60%  $\alpha$ -chloronaphthalene at 350°. Approximately 15–20% of dichloronaphthalene is formed. At 400° the reaction products are destroyed. In the presence of 0.5% iodine, the formation of mono-substituted products is favoured, whilst ferric chloride, porous earthenware, or wood charcoal activates the production of both mono- and poly-substituted derivatives (Ferrero and Wunenburger, *l.c.*).



A particularly detailed study of the chlorination of naphthalene in solvents with the object of obtaining the highest yield of  $\alpha$ -chloronaphthalene has been made by Ferrero and his collaborators, who do not agree with Traubenberg and Wasserman (J. pr. Chem. 1928, [ii], 120, 177) that chlorination in cold benzene in presence of ferric chloride gives the best yield. With Fehlmann (1929) and Corbaz (1930, *l.c.*) Ferrero studied chlorination in a large number of solvents, including benzene, chlorobenzene, *o*- and *p*-dichlorobenzene, decalin, toluene, ethyl alcohol, acetic acid, ethyl acetate, tetra- and penta-chloroethane and carbon tetrachloride; they compared the effects of using iodine ( $\frac{1}{2}\%$ ) or ferric chloride ( $\frac{1}{2}\%$ ) with those obtained without catalyst. The most favourable results were obtained with benzene, chlorobenzene, and acetic acid, solvents which are protected from chlorine attack by the naphthalene; solvents which themselves tend to protect the naphthalene from attack, such as toluene and carbon tetrachloride, lead to formation of polychloronaphthalenes. Iodine as catalyst favours monochlorination of naphthalene whilst ferric chloride produces more polychlorination. A higher temperature favours monochlorination. Using benzene or chlorobenzene with iodine as catalyst at a temperature near the boiling-point of the solvent, a 92% yield of  $\alpha$ -chloronaphthalene is obtained; the remainder is mainly di- and tri-chloronaphthalenes. The process employing benzene and chlorobenzene was patented by Ferrero and Fehlmann (Swiss. P. 134089, 1928).

$\alpha$ -Chloronaphthalene (m.p.  $-25^\circ$ , b.p.  $259.3^\circ$ ,  $d_4^{15}$  1.2025) is prepared as indicated above. It can be isolated and purified by fractional distillation, or by cooling the crude product to  $-15^\circ$  when pure  $\alpha$ -chloronaphthalene separates (Britton, Reed, and the Dow Chemical Co., U.S.P. 1917822). By cooling an alcoholic solution of the residue to  $-40^\circ$ , pure  $\beta$ -chloronaphthalene is obtained. The eutectic of  $\alpha$ - and  $\beta$ -chloronaphthalenes, containing 25% of  $\alpha$ -, melts at  $-18^\circ$  (*ibid.*). Other methods of preparation are from  $\alpha$ -naphthylamine through the diazo-compound, and by decomposition of naphthalene dichloride (Faust and Saame, Annalen, 1871, 160, 68; Armstrong and Wynne, Proc. C.S. 1890, 6, 85).

$\alpha$ -Chloronaphthalene has found no technical use.

$\beta$ -Chloronaphthalene (m.p.  $56^\circ$ , b.p.  $264.3^\circ$ ) is prepared by heating  $\beta$ -naphthol with 1.5 mol. phosphorus pentachloride (Berger, Compt. rend, 1905, 141, 1027; Cleve and Juhlin-Dannfelt, Bull. Soc. chim. 1876, [ii], 25, 258) and by other standard methods. It may also be isolated from the products of monochlorination of naphthalene after separation of  $\alpha$ -chloronaphthalene (*v. supra*).

#### DICHLORONAPHTHALENES.

The principal dichloronaphthalenes are the 1:4- and 1:5-isomers and they are formed in admixture when naphthalene in carbon tetrachloride solution is chlorinated at  $-10^\circ$  to  $0^\circ$  with iodine or ferric chloride as catalyst. The chlorination mass contains small quantities of the 1:2- and 1:7-isomers which can be removed

as sulphonic acids by stirring in the cold with sulphuric acid for 20 hours (Badische, G.P. 234912).

1:4-Dichloronaphthalene can be made by chlorinating 1-chloronaphthalene-8-sulphonic acid at  $250^\circ$  to give 1:4-dichloronaphthalene-8-sulphonic acid and removing the sulphonic group by hydrolysis (I.G., B.P. 341926). Another method is to heat naphthalene with sulphuryl chloride at  $140$ – $160^\circ$  when an almost pure product is obtained in 70% yield (Höchst, G.P. 286489) or naphthalene is heated with thionyl chloride (Meyer, Monatsh. 1915, 36, 728).

1:5-Dichloronaphthalene can be made by acid hydrolysis of 1:5-dichloronaphthalene-2-sulphonic acid (Cleve, Chem.-Ztg. 1893, 17, 398).

1:6-Dichloronaphthalene is the main product of chlorination of sodium naphthalene- $\alpha$ -sulphonate in hydrochloric acid with potassium chlorate (Koslov and Talybov, J. Gen. Chem. Russ. 1939, 9, 1827; Amer. Chem. Abstr. 1940, 34, 4067).

Octachloronaphthalene or perchloronaphthalene,  $C_{10}Cl_8$ , m.p.  $198^\circ$ , can be produced by exhaustive chlorination of naphthalene in presence of a suitable catalyst (Berthelot and Jungfleisch, Bull. Soc. chim. 1868, [ii], 9, 446) or by heating sodium  $\alpha$ -naphthylamine-3:6:8-trisulphonate with phosphorus pentachloride at  $200$ – $225^\circ$  (Schvemberger and Gordon, J. Gen. Chem. Russ. 1932, 2, 921). It is attacked by alcoholic but not by aqueous alkalis, and converted by nitric acid to hexachloronaphthalene and tetrachlorophthalic acid. Further chlorination of octachloronaphthalene gives decachlorohydrindene (Schvemberger and Gordon, *l.c.*).

#### Properties of the Chloronaphthalenes.

Except  $\alpha$ -chloronaphthalene, which is a liquid, the chlorinated naphthalenes are solid crystalline bodies with melting-points ranging from  $35^\circ$  for 1:2-dichloronaphthalene to  $198^\circ$  for octachloronaphthalene. Boiling-points range from  $259.3^\circ$  for  $\alpha$ -chloronaphthalene to  $440$ – $442^\circ$  for octachloronaphthalene. The melting-points and known boiling-points are given in the Table shown on the opposite page.

In addition, Turner and Wynne (J.C.S. 1941, 243) give the melting-points of seven more of the tetrachloronaphthalenes in which the relative positions of three of the four chlorine atoms have been determined, as follows:

Constitution.	M.p.
1:2:5:7- . . . .	$164^\circ$
1:2:5:7- . . . .	$110^\circ, 114^\circ$
1:2:7:7- . . . .	$144^\circ$
1:2:8:7- . . . .	$135^\circ$
1:4:7:7- . . . .	$109^\circ$
1:4:8:7- . . . .	$144^\circ$
3:6:7:7- . . . .	$218^\circ$

The chlorinated naphthalenes are of a high degree of chemical stability. Concentrated sulphuric acid at elevated temperatures converts them to chloronaphthalenesulphonic acids, and oxidation by nitric acid gives the corresponding chloro-substituted phthalic acids. The course of oxidation by chromic acid in acetic acid depends on the position of the chlorine atoms; 1:5-di-



(Beattie and Whitmore, J. Amer. Chem. Soc. 1933, 55, 1546).

2. By sulphonation of the mono- or polychloronaphthalenes, when a mixture of isomers of more or less complexity is obtained, monosulphonic being accompanied by disulphonic acids.
3. By chlorination of naphthalenesulphonic acids, the chlorine atom entering an  $\alpha$ -position.

(For  $\alpha$ -chloronaphthalene-2- and 3-sulphonyl chlorides, see pp. 303d, 304a.)

(i)  $\alpha$ -(or 1-)Chloronaphthalene-4-sulphonic Acid is formed as chief product when  $\alpha$ -chloronaphthalene interacts with chlorosulphonic acid in the cold (Armstrong and Wynne, Proc. C.S. 1890, 6, 86). With excess chlorosulphonic acid  $\alpha$ -chloronaphthalene-4-sulphonyl chloride is formed (Ferrero and Bolliger, Helv. Chim. Acta, 1928, 11, 1144).  $\alpha$ -Chloronaphthalene sulphonated with monohydrate gives a maximum yield of 70% of  $\alpha$ -chloronaphthalene-4-sulphonic acid at 56°, the amount decreasing with higher temperature of reaction to 31% yield at 98°. The 5-isomer could not be detected but at 160° some 6-isomer was formed (Ferrero and Bolliger, l.c.).

*Properties.*—The chloride has m.p. 95° and the amide m.p. 187° (Cleve, Ber. 1887, 20, 73). The solubility of the Na, K, Ca, Ba salts at 18° are 1.79, 0.73, 0.19, 0.08, and at 98° are 40, 40, 0.84, and 0.46 g. per 100 c.c. water respectively. The barium salt,  $\text{BaA}_2 + 2\text{H}_2\text{O}$ , crystallises as hexagonal plates and the potassium salt, KA, as rhombic prisms.  $\alpha$ -Chloronaphthalene-4-sulphonic acid is converted by caustic soda to  $\alpha$ -naphthol-4-sulphonic acid and by ammonia to  $\alpha$ -naphthylamine-4-sulphonic acid.

(ii)  $\alpha$ -Chloronaphthalene-5-sulphonic Acid is the chief product when  $\alpha$ -chloronaphthalene interacts with chlorosulphonic acid first in the cold and finally at 150° (Armstrong and Wynne, Proc. C.S. 1890, 6, 87). It can be obtained by chlorinating sodium naphthalene- $\alpha$ -sulphonate with sodium chlorate and hydrochloric acid (Rudolph, G.P. 103983, B.P. 19088, 1898). It is not formed in the sulphonation of  $\alpha$ -chloronaphthalene with sulphuric acid (Ferrero and Bolliger, l.c.).

*Properties.*—The chloride has m.p. 95° and the amide m.p. 226° (Cleve, Ber. 1887, 20, 73). The water of crystallisation and solubility at 20° of some of the salts of  $\alpha$ -chloronaphthalene-5-sulphonic acid, in g. per 100 c.c. water are as follows: Ca+ $\text{H}_2\text{O}$ , 0.37; Sr+ $3\text{H}_2\text{O}$ , 0.55; Ba+ $2\text{H}_2\text{O}$ , 0.27; Zn+ $4\text{H}_2\text{O}$ , 1.20; Mn+ $\text{H}_2\text{O}$ , 0.74; Co+ $4\text{H}_2\text{O}$ , 0.71; Ni+ $4\text{H}_2\text{O}$ , 0.62; Cu+ $4\text{H}_2\text{O}$ , 1.09; Pb+ $2\text{H}_2\text{O}$ , 0.20; Ag anhyd., 0.55 (Ephraim and Pfister, Helv. Chim. Acta, 1925, 8, 229).  $\alpha$ -Chloronaphthalene-5-sulphonic acid is converted by caustic soda to  $\alpha$ -naphthol-5-sulphonic acid and by ammonia to  $\alpha$ -naphthylamine-5-sulphonic acid.

(iii)  $\alpha$ -Chloronaphthalene-6-sulphonic Acid is produced along with the 7-sulphonic acid when  $\alpha$ -chloronaphthalene is heated with 1-1.5 times its weight of sulphuric acid at 160-170° (Oehler, G.P. 76396; Ferrero and Bolliger, l.c.); or by chlorination of sodium naphthalene-

$\beta$ -sulphonate with chlorine or with sodium chlorate and hydrochloric acid (Rudolph, G.P. 101349; B.P. 19088, 1898).

*Properties.*—The chloride has m.p. 114-115° and the amide m.p. 216° (Cleve, Ber. 1887, 20, 73). The barium salt,  $\text{BaA}_2 + \text{H}_2\text{O}$  and the potassium salt, KA, are only sparingly soluble in cold water and so permit of separation from the salts of the more soluble 7-sulphonic acid.

(iv)  $\alpha$ -Chloronaphthalene-7-sulphonic Acid is prepared from a  $\alpha$ -naphthylamine-7-sulphonic acid by the Sandmeyer reaction (Cleve, *ibid.* 1892, 25, 2480) or together with the 6-sulphonic acid by sulphonation of  $\alpha$ -chloronaphthalene. The chloride has m.p. 94° and the amide m.p. 185-186°.

(v)  $\alpha$ -Chloronaphthalene-8-sulphonic Acid has been prepared in the form of its chloride by interaction of potassium  $\alpha$ -nitronaphthalene-8-sulphonate with phosphorus pentachloride (Cleve, *ibid.* 1890, 23, 962). The chloride has m.p. 101° and the amide m.p. 196-197°.

(vi)  $\alpha$ -Chloronaphthalene-3:6-disulphonic Acid is obtained by chlorination of naphthalene-2:7-disulphonic acid (Rudolph, G.P. 103983). It has been prepared by Sandmeyer reaction from  $\alpha$ -naphthylamine-3:6-disulphonic acid (Armstrong and Wynne, Proc. C.S. 1895, 11, 82). The chloride is dimorphous, the two forms having the m.ps. 115° and 127° respectively.

(vii)  $\alpha$ -Chloronaphthalene-3:8-disulphonic Acid has been prepared from  $\alpha$ -naphthylamine-3:8-disulphonic acid by Sandmeyer reaction (Armstrong and Wynne, Proc. C.S. 1890, 6, 16). The chloride has m.p. 110°.

(viii)  $\alpha$ -Chloronaphthalene-4:6-disulphonic Acid is formed by sulphonation of  $\alpha$ -chloronaphthalene-6-sulphonic acid at 100° (Rudolph, G.P. 104902). It has also been made from  $\alpha$ -naphthylamine-4:6-disulphonic acid by the Sandmeyer reaction (Armstrong and Wynne, Proc. C.S. 1890, 6, 126). Fusion with caustic soda at 230° produces 1:6-dihydroxynaphthalene-4-sulphonic acid (Rudolph, l.c.).

(ix)  $\alpha$ -Chloronaphthalene-4:7-disulphonic Acid is obtained by sulphonating  $\alpha$ -chloronaphthalene with 45% oleum at 20°, or with sulphuric acid at 180° (Oehler, G.P. 74744); or by sulphonating  $\alpha$ -chloronaphthalene-4-sulphonic acid with 20% oleum at 20° (Oehler) or at 100° (Armstrong and Wynne, Proc. C.S. 1890, 6, 18). The chloride has m.p. 107°.

(x)  $\alpha$ -Chloronaphthalene-4:8-disulphonic Acid has been made by the Sandmeyer reaction from  $\alpha$ -naphthylamine-4:8-disulphonic acid (Armstrong and Wynne, l.c., p. 126). The chloride has m.p. 135°.

(xi)  $\alpha$ -Chloronaphthalene-2:4:7-trisulphonic Acid is formed by sulphonation of  $\alpha$ -chloronaphthalene with 45% oleum or by sulphonation of  $\alpha$ -chloronaphthalene-4-sulphonate with 20% oleum at 170° (Oehler, G.P. 76230). The chloride has m.p. 215° (Armstrong and Wynne, Proc. C.S. 1890, 6, 126).

(xii)  $\beta$ -Chloronaphthalene-6-sulphonic Acid is the main product when  $\beta$ -chloronaphthalene is sulphonated with oleum at 180° and is separated from accompanying 8-sulphonic acid

by the sparingly soluble lead salt (Arnell, Bull. Soc. chim. 1881, [ii], 45, 184). It has been produced also by the Sandmeyer reaction from  $\beta$ -naphthylamine-6-sulphonic acid. The chloride has m.p. 110° and amide m.p. 183°.

(xiii)  $\beta$ -Chloronaphthalene-8-sulphonic Acid is formed along with the 6-sulphonic acid when  $\beta$ -chloronaphthalene is sulphonated at 100° with oleum (*idem, ibid.*), or by the action of chlorosulphonic acid in the cold on  $\beta$ -chloronaphthalene in carbon disulphide solution (Armstrong and Wynne, Proc. C.S. 1888, 4, 105). The following  $\beta$ -chloronaphthalenesulphonic acids have been prepared by the Sandmeyer reaction from the corresponding  $\beta$ -naphthylaminesulphonic acids:

(xiv)  $\beta$ -Chloronaphthalene-1-sulphonic Acid.—Chloride, m.p. 76°; amide, m.p. 153° (*idem, ibid.* 1895, 11, 238).

(xv)  $\beta$ -Chloronaphthalene-5-sulphonic Acid.—Chloride, m.p. 69°; amide, m.p. 214° (*idem, ibid.* 1889, 5, 48).

(xvi)  $\beta$ -Chloronaphthalene-7-sulphonic Acid.—Chloride, m.p. 86.5°; amide, m.p. 176° (*idem, ibid.*, p. 49).

The  $\beta$ -chloronaphthalenedisulphonic acids are only of academic interest and have usually been prepared by the Sandmeyer reaction on the corresponding  $\beta$ -naphthylaminedisulphonic acids (*idem, ibid.* 1890, 6, 127, 130; 1891, 7, 27).

#### BROMO- AND IODO-NAPHTHALENES.

Bromination of naphthalene has been studied by a number of workers, some of whom are referred to below under individual compounds. Direct bromination gives mainly  $\alpha$ -bromonaphthalene, together with 1:4- and 1:5-dibromonaphthalenes. Bromo-derivatives of naphthalene can also be obtained by replacing other substituents such as amino-, hydroxy-, and nitro- groups in the naphthalene nucleus, by standard methods.

$\alpha$ -Bromonaphthalene.—A method for brominating naphthalene in carbon tetrachloride solution to give a 72–75% yield of  $\alpha$ -bromonaphthalene is described in Organic Syntheses, 1930, 10, 14. It can also be prepared by the action of sulphur bromide in benzene (Edinger and Goldberg, Ber. 1900, 33, 2885) or of iodine monobromide (Melitzer, J. Amer. Chem. Soc. 1938, 60, 256) on naphthalene, among other methods.

$\alpha$ -Bromonaphthalene is a colourless oil with a characteristic odour, m.p.  $6.2 \pm 0.02^\circ$  (Jones and Lapworth, J.C.S. 1914, 105, 1804), 6.1° (Timmermans and Hennaut-Roland, J. Chim. phys. 1937, 34, 693), b.p. 281.1° (Kahlbaum and Arndt, Z. physikal. Chem. 1898, 26, 627),  $\rho_4^{25}$  1.4785,  $n_D^{20}$  1.6582 (Jones and Lapworth, *l.c.*).

$\beta$ -Bromonaphthalene is obtained from  $\beta$ -naphthylamine *via* the diazo-compound, especially by heating the complex formed by the bromide of the latter with mercuric bromide (Schwechten, Ber. 1932, 65 [B], 1605; Newman and Wise, J. Amer. Chem. Soc. 1941, 63, 2847). Several workers have made it from  $\beta$ -naphthol and phosphorus tribromide. It has m.p. 58–59°; b.p. 281–282° (Sah, Rec. trav. chim. 1940, 59, 1021).

1:2-Dibromonaphthalene, from 1-bromo-2-

aminonaphthalene, has m.p. 67–68° (Meldola and Streatfeild, J.C.S. 1893, 63, 1054).

1:3-Dibromonaphthalene, m.p. 64° (Meldola, Ber. 1879, 12, 1963).

1:4-Dibromonaphthalene has m.p. 82–83° (Goldstein and Stern, Helv. Chim. Acta, 1940, 23, S09). Its formation in the bromination of naphthalene has been studied by Zalkind and Faerman (J. Russ. Phys. Chem. Soc. 1930, 62, 1021).

1:5-Dibromonaphthalene, m.p. 131°, has been obtained in 19% yield in the bromination of naphthalene (Zalkind and Faerman, *l.c.*).

1:6-Dibromonaphthalene has m.p. 61° (Claus and Philipson, J. pr. Chem. 1891, [ii], 43, 51; Armstrong and Rossiter, Proc. C.S. 1891, 7, 184).

1:7-Dibromonaphthalene, m.p. 75°, by brominating  $\beta$ -bromonaphthalene (*idem, ibid.*; cf. Forsling, Ber. 1889, 22, 619, 1402).

1:8-Dibromonaphthalene, m.p. 108.5–109°, from 8-bromo- $\alpha$ -naphthylamine (Meldola and Streatfeild, *l.c.*).

2:3-Dibromonaphthalene, m.p. 140°, from 3-bromo- $\beta$ -naphthylamine (Wynne, Proc. C.S. 1914, 30, 204; Kenner, Ritchie, and Wain, J.C.S. 1937, 1526).

2:6-Dibromonaphthalene, m.p. 158°, from 6-bromonaphthalene- $\beta$ -sulphonyl bromide (Forsling, *l.c.*, p. 1401).

2:7-Dibromonaphthalene, m.p. 140–141° (Franzen and Stäuble, J. pr. Chem. 1921, [ii], 101, 58), from 3:6-dibromo-2-naphthylamine.

Several tri- and tetra-bromonaphthalenes have been described; only the most recent references are given below:

1:2:4-Tribromonaphthalene, m.p. 112–113° (Consdon and Kenyon J.C.S. 1935, 1596).

1:2:6-Tribromonaphthalene, m.p. 118° (Claus and Philipson, *l.c.*).

1:4:5-Tribromonaphthalene, m.p. 85° (Jolin, Bull. Soc. chim. 1877, [ii], 28, 514).

1:4:6-Tribromonaphthalene, m.p. 86–87°. Zalkind and Belikov obtained it in the bromination of  $\alpha$ -bromonaphthalene (Ber. 1931, 64 [B], 955).

1:3:6-Tribromonaphthalene, m.p. 98°, from 1:3:6-tribromo- $\beta$ -naphthylamino (Franzen and Stäuble, J. pr. Chem. 1921, [ii], 101, 58).

1:2:3:4-Tetrabromonaphthalene, m.p. 196°, from 1:3:4-tribromo- $\beta$ -naphthylamine (Hodgson and Hathway, J.C.S. 1944, 21).

1:4:6:7-Tetrabromonaphthalene, m.p. 173–174°, from 1:4-dibromonaphthalene tetrabromido (Guareschi, Gazzetta, 1886, 16, 146); another isomer, 1:4:x:x, m.p. 119–120°, was obtained at the same time.

Hexabromonaphthalenes.—By brominating naphthalene in presence of aluminium bromide, Zelinsky and Turova-Pollak obtained a hexabromonaphthalene, m.p. 312°, identical with the product obtained similarly from *cis*-decalin. *trans*-Decalin, however, gave a hexabromonaphthalene, m.p. 269° (Ber. 1929, 62 [B], 1658). Earlier workers described products, m.p. 245–246° (Gessner, *ibid.* 1876, 9, 1510) and 252° (Roux, Ann. Chim. Phys. 1887, [vi], 12, 347).

Isomerisation of Bromonaphthalenes.— $\alpha$ -Bromo- is converted into  $\beta$ -bromo-naphthalene

by the action of aluminium chloride in carbon disulphide solution (Roux, *l.c.*; Fisher and Clark, *Canad. J. Res.* 1939, 17, B, 251) and by passage over silica gel in a current of air at 350° (Mayer and Schiffrin, *Ber.* 1934, 67 [B], 67). 1:2-Dibromonaphthalene has been converted by the action of aluminium chloride in presence of acetyl chloride into 1:4-, 1:5-, and 2:6-dibromonaphthalenes (Lohfert, *ibid.* 1930, 63 [B], 1939).

#### Iodonaphthalenes.

$\alpha$ -Iodonaphthalene, has been prepared by several workers and is described as a thick oil, b.p. 305°. For the direct iodination of naphthalene, see Birckenbach and Goubeau, *ibid.* 1932, 65 [B], 395; Varma *et al.*, *J. Indian Chem. Soc.* 1933, 10, 595).

$\beta$ -Iodonaphthalene, m.p. 53–54°, b.p. 172°/21 mm. (Schmidlin and Huber, *Ber.* 1910, 43, 2829). 1:2-Di-, m.p. 81°, and 1:4-di-iodonaphthalene, m.p. 109–110°, were prepared by Meldola (*J.C.S.* 1885, 47, 522), and 1:8-di-iodonaphthalene, m.p. 109°, by Scholl, Seer, and Weitzenbock (*Ber.* 1910, 43, 2207).

#### NAPHTHALENESULPHONIC ACIDS.

The mono-, di-, and tri-sulphonic acids of naphthalene are important dyestuff intermediates and the sulphonation process is therefore of major technical importance. The number of different acids which can be formed by direct sulphonation of naphthalene is restricted to the two mono-, four di-, and three tri-sulphonic acids. The products obtained depend on the nature, quantity, and concentration of the sulphonating agent,\* on temperature and on time, and are summarised in a number of rules. A low temperature and a mild sulphonating agent such as chlorosulphonic acid favour sulphonation in the  $\alpha$ -position, high temperature the  $\beta$ -position; excess of reagent promotes polysulphonation; disulphonic acids formed are always heteronuclear†; a second sulphonic group takes up a position as remote as possible from the first, thus, low-temperature sulphonation of the  $\beta$ -mono-acid gives 1:6- and not 1:7-disulphonic acid.‡ At high temperatures  $\alpha$ -sulphonic groups move into  $\beta$ -positions if such movement is compatible with the rule that two sulphonic groups do not take up adjacent positions. The phenomenon of isomeric change of sulphonic acids has already been discussed (p. 271a).

The course of sulphonation, ignoring isomerisation effects is summarised in the diagram opposite, where S represents the  $\text{SO}_3\text{H}$  group.

#### NAPHTHALENE MONOSULPHONIC ACIDS.

The conditions leading to the formation of naphthalene- $\alpha$ - and  $\beta$ -sulphonic acids, which were first studied by Merz and Weith (*ibid.* 1870, 3, 195) have already been reviewed in detail (p. 271a) in the discussion on isomeric change.

Various methods have been employed for the

\* Cf. footnote, p. 271b.

† It has been stated that the 1:3-acid is also formed (g.v.).

‡ The formation of 1:7 disulphonic acid in the sulphonation of naphthalene at 130° (>25%) has been reported by Fierz-David and Richter (*Helv. Chim. Acta*, 1945, 28, 257) and of naphthalene- $\beta$ -sulphonic acid by Lantz (*Bull. Soc. chim.* 1945, [v], 12, 262).

determination of naphthalene- $\alpha$ - and  $\beta$ -monosulphonic acids in presence of each other. Lantz (*Bull. Soc. chim.* 1935, [v], 2, 1913) has devised a method in which bromine reacts with the mixture under specific conditions whereby the  $\beta$ -isomer is brominated to give a soluble product, whilst the  $\alpha$ -isomer undergoes replacement of the sulphonic-group to give an insoluble product. The proportion of the  $\alpha$ -isomer can be determined by measurement of the sulphuric acid formed or by chromic acid oxidation of the insoluble bromo-compound. Terentiev (*Sci. Rep. Moscow State Univ.* 1936, No. 6, 199; *Amer. Chem. Abstr.* 1938, 32, 4104) estimates naphthalene- $\alpha$ -sulphonic acid by interaction with sodium amalgam, when the sulphonic group is removed as sodium sulphite which is then determined. This method should be employed with reserve since in all probability the group will also be eliminated from naphthalene- $\beta$ -sulphonic acid to some degree. The effect of having disulphonic acids present may lead to error, though it is stated that under the conditions employed the groups in naphthalene-1:5-disulphonic acid are only slightly attacked but with naphthalene-1:6-disulphonic acid one sulphonic-group is removed. Kiprianov (*Zavod. Lab.* 1934, 3, 414; *B.* 1934, 823) estimated naphthalene- $\beta$ -sulphonic acid by precipitation as the sparingly soluble magnesium salt. Euwes (*Rec. trav. chim.* 1909, 28, 304) devised a method of analysis depending on the mutual solubility effects of the lead salts of naphthalene- $\alpha$ - and  $\beta$ -sulphonic acids and from a predetermined curve it was possible to determine the proportion of  $\alpha$ -isomer in a mixture of  $\alpha$ - and  $\beta$ -isomers.

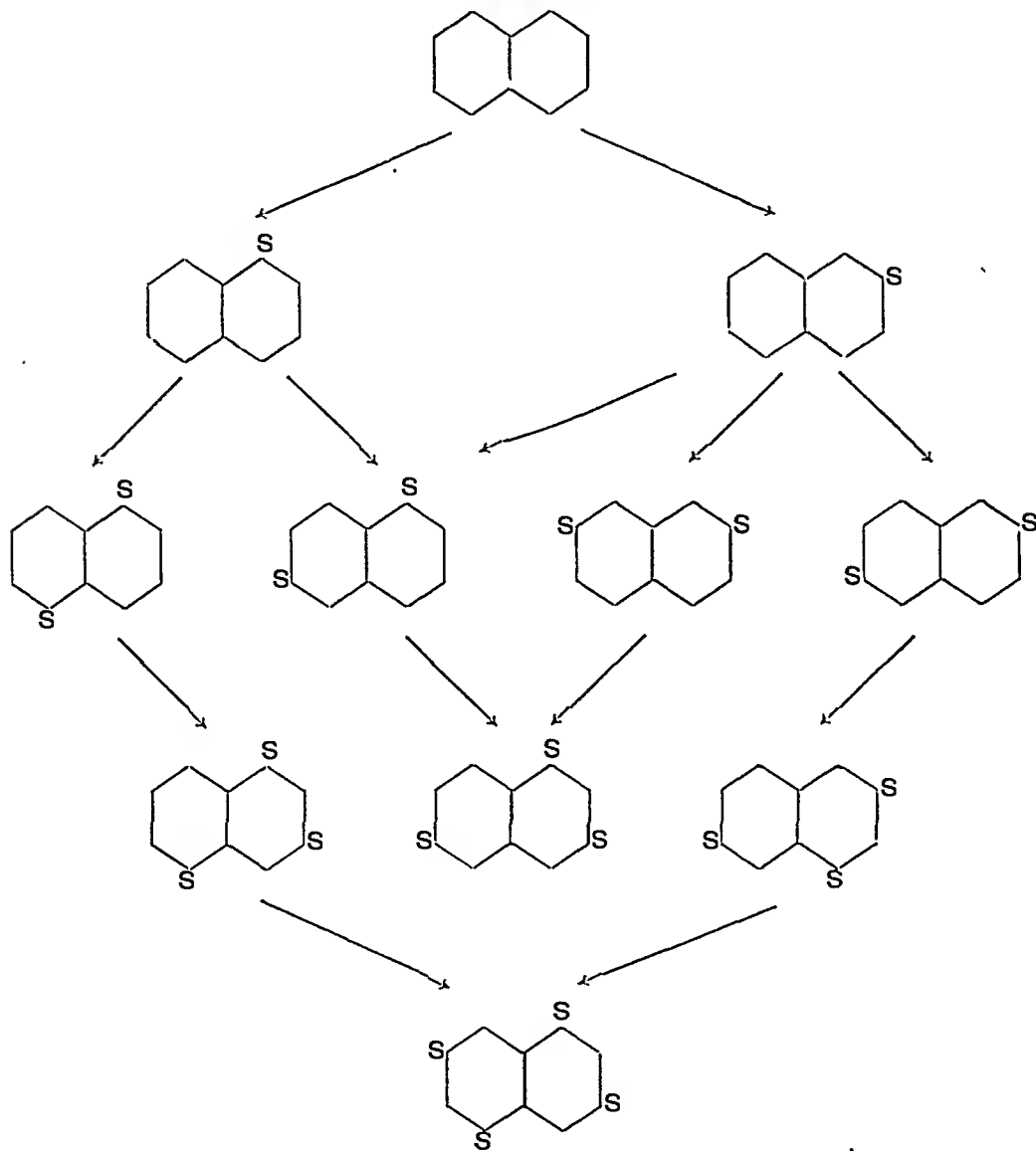
This last method was also used by Witt in his study of the monosulphonation of naphthalene (*Ber.* 1915, 48, 754). Witt developed the method of sulphonation of naphthalene to give mainly the  $\beta$ -isomer in which naphthalene is heated to about 160°, the sulphuric acid is added over a short period of time and the reaction mass then heated until sulphonation is complete. By heating 250 g. naphthalene to 160° and adding 400 g. of 93.7% sulphuric acid (160% of theory) during 15 minutes and finally maintaining for 15 minutes at 160°, Witt found 85%  $\beta$ -isomer formed and 15%  $\alpha$ -isomer and a small formation (less than 1%) of dinaphthylsulphone. Although this may be the proportion of isomers formed under the above conditions, the manufacturing methods produce much less  $\alpha$ -isomer than 15%. In a typical manufacturing procedure in which naphthalene is heated at 165°, 1–1.25 mol. monohydrate added and the reaction mass heated 2–3 hours at 165°, there will be 13–15% of naphthalene unsulphonated, 1–2% of dinaphthylsulphone formed, 80–81% of naphthalene- $\beta$ -sulphonic acid and the remaining 4–5% will consist of  $\alpha$ -isomer and any disulphonic acids formed (private communication). Under these conditions therefore the proportion of  $\alpha$ - to  $\beta$ -isomer is far less than the ratio 15:85 found by Witt.

Naphthalene- $\alpha$ -sulphonic Acid is obtained by sulphonation of naphthalene at temperatures not above 70°. Finely powdered naphthalene is added with stirring to 1.5–2 parts by weight of sulphuric acid at 40–50°, the temperature finally

being raised to 70° to complete the sulphonation. The naphthalene- $\alpha$ -sulphonic acid may be isolated as sodium salt either by neutralising with lime and converting the resulting solution of the filtered calcium salt to sodium salt by addition of sodium carbonate or by addition of salt to the diluted sulphonation mass (G.P. 50411).

An alternative separation designed to ensure freedom from  $\beta$ -isomer is described in B.P.

414573 (Geigy) in which to the diluted sulphonation product is added sufficient ferrous salt to precipitate the  $\beta$ -isomer as the sparingly soluble ferrous salt and, after filtration, sodium naphthalene- $\alpha$ -sulphonate is isolated from the filtrate by addition of salt. According as the temperature of sulphonation is varied from 20° to 65°, the proportion of  $\alpha$ -isomer varies from 90% to 85% and the proportion of  $\beta$ -isomer from 10% to 15%. The above method of isolation



results in separation of 90% of the  $\alpha$ -isomer present and the product contains only 0.5–1% of  $\beta$ -isomer.

Naphthalene- $\alpha$ -sulphonic acid has been prepared in pure form by sulphonating naphthalene with 2 parts by weight of acid at 0° and after inducing the sulphonic acid to crystallise from the sulphonation mass, the filtered  $\alpha$ -isomer, which contains naphthalene, is purified by solution in water, filtration from naphthalene and concentration of the filtrate under vacuum at 35° to a density of 1.29–1.3. On cooling,  $\alpha$ -acid separates as a crystalline mass, which can be further purified by solution in water and

precipitation from concentrated solution by hydrogen chloride (Fierz and Weissenbach, *Helv. Chim. Acta*, 1920, 3, 314).

*Identification.*—The acid,  $\text{HA} \cdot 2\text{H}_2\text{O}$ , forms easily soluble, non-deliquescent crystals (m.p. 90°) which cannot be dehydrated without decomposition. The ammonium salt,  $\text{NH}_4\text{A}$ , and the zinc, cobalt, nickel, copper, and cadmium salts, each having 6 mol. water of crystallisation, are described by Fierz and Weissenbach (*l.c.*)

The chloride has m.p. 67° (Erdmann and Stüvorn, *Annalen*, 1893, 275, 235) and the amide m.p. 150° (Maikopar, *Zeit. Chem.* 1869, [ii], 5, 711). The benzyl- $\omega$ -thiocarbamide salt is a well-



defined crystalline product, m.p. 136.8° (Chambers and Watt, J. Org. Chem. 1941, 6, 376; see also Chambers and Scherer, Ind. Eng. Chem. 1924, 16, 1272; Hann and Keenan, J. Physical Chem. 1927, 31, 1082).

The solubility of a number of salts of naphthalene- $\alpha$ -sulphonic acid has been determined by Ephraim and Seger (Helv. Chim. Acta, 1925, 8, 724). All the following salts have 6 mol. water of crystallisation, and the solubilities (at 17°) are expressed in g. of anhydrous salt per litre: *magnesium* 69.78, *cobalt* 64.17, *nickel* 49.78, *copper* 46.47, *cadmium* 45.08, *zinc* 6.59, *manganese* 4.79.

**Reactions and Uses.**—Further sulphonation at low temperature is an important reaction leading to the formation of *naphthalene-1:5-disulphonic acid* together with some 1:6-isomer. Another technically important reaction is nitration, by which is mainly formed  *$\alpha$ -nitronaphthalene-8-sulphonic acid* together with some 5-isomer. Fusion of naphthalene- $\alpha$ -sulphonic acid with caustic soda produces  *$\alpha$ -naphthol*.

Naphthalene- $\beta$ -sulphonic Acid is prepared by adding sulphuric acid to an equal weight of naphthalene at 160°, and after 3 hours at this temperature heating for 1 hour at 170° and then for 1 hour at 180°. The product is usually isolated as sodium salt by addition of salt to the diluted sulphonation mass or the diluted acidic mass may be neutralised with sodium carbonate and the  $\beta$ -salt isolated by addition of salt. Sodium sulphate or sodium sulphite may be used for the isolation (Uhlmann, G.P. 229537). In manufacture it is usual to employ less severe conditions of sulphonation so as to minimise formation of disulphonic acids and dinaphthylsulphone, and there remains in the sulphonation mass a small quantity of naphthalene which after dilution of the mass is removed by steam distillation (*v. supra*).

If the sulphonation mass is only diluted to a small extent so that the boiling-point is 145–155°, then by distillation not only is free naphthalene removed but also naphthalene- $\alpha$ -sulphonic acid is hydrolysed back to naphthalene (Nat. Aniline and Chem. Co., Inc., U.S.P. 1922813).

Grischen and Spryskov (Anilinokras Prom. 1932, 2, No. 11, 19; Amer. Chem. Abstr. 1933, 27, 4791) have sulphonated naphthalene to give the  $\beta$ -sulphonic acid by heating 0.7 mol. naphthalene with 1 mol. sulphuric acid at 155°, and when sulphonation is complete applying vacuum to remove water and so concentrate the residual sulphuric acid; 0.2 mol. naphthalene is now added at 155° and the mass similarly treated and finally the remaining 0.1 mol. naphthalene is added.

Spryskov (J. Chem. Ind. Russ. 1931, 8, 41; B. 1932, 378) has obtained 97% sulphonation by sulphonating naphthalene with 1 mol. sulphuric acid at 160°, removing the water of reaction by passing in benzine vapour purified by treatment with sulphuric acid. Spryskov attributes the inferior results obtained by Gay using a similar method to the use of impure ligroin (Chim. et Ind. 1928, 19, 387).

Fierz-David and Blangey, "Farbenchemie," 4th ed., p. 133, give details of a method for

making and isolating naphthalene- $\beta$ -sulphonic acid (sodium salt). 256 g. naphthalene is heated to 165° and 280 g. 94% sulphuric acid added during 30 minutes, after which the reaction mass is heated 1 hour at 165°, 1 hour at 167°, 1 hour at 170°, and finally 1 hour at 173° during which time 25 g. naphthalene and 30 g. water distil over. The reaction mass is poured into 1,800 c.c. water, partially neutralised by addition of 60 g. sodium carbonate followed by 360 g. salt whereby the  $\beta$ -salt is precipitated; after cooling and stirring the suspension for some hours it is filtered off and dried. The actual yield of dried product is 400–420 g., and it can be used for direct fusion to  $\beta$ -naphthol.

Naphthalene- $\beta$ -sulphonic acid can be isolated as the free acid in the form of its crystalline trihydrate by suitable dilution with water of a naphthalene- $\beta$ -sulphonation mass. Witt (Ber. 1915, 48, 755) heated 250 g. naphthalene at 160° with 400 g. 93.7% sulphuric acid and diluted the sulphonation mass with 300 c.c. water. The  $\beta$ -acid separates as a crystalline mass and may be purified from a small amount of dinaphthylsulphone by solution of 600 g. of the product in 300 c.c. water at 70°, filtering from sulphone and precipitating the naphthalene- $\beta$ -sulphonic acid as its trihydrate by adding 100 c.c. hydrochloric acid and cooling.

**Identification.**—The acid,  $\text{HA} + 3\text{H}_2\text{O}$ , forms non-deliquescent lustrous scales, m.p. 83°, from which the monohydrate, m.p. 142°, and the anhydrous product, m.p. 91°, can be prepared. The anhydrous product is soluble in toluene (Witt, *loc.*). The chloride has m.p. 79° (Fischer and Bergell, *ibid.* 1902, 35, 3779) and the amide m.p. 217° (Cleve, Bull. Soc. chim. 1876, [ii], 25, 258). The *benzyl- $\psi$ -thiocarbamide* salt is a well-defined crystalline product, m.p. 190.5° (Chambers and Watt, J. Org. Chem. 1941, 6, 376; cf. Chambers and Scherer, Ind. Eng. Chem. 1924, 16, 1272; Hann and Keenan, J. Physical Chem. 1927, 31, 1082).

The water of crystallisation and the solubility of many salts in g. of anhydrous salt per 100 c.c. water (mostly at 16.5°) have been determined by Ephraim and Pfister (Helv. Chim. Acta, 1925, 8, 229):  $\text{NH}_4\text{A}$ , anhyd. 13.14 at 25°;  $\text{NaA}$ , anhyd. 5.67 at 25°;  $\text{KA} + \frac{1}{2}\text{H}_2\text{O}$ , 8.02;  $\text{MgA}_2 + 4\text{H}_2\text{O}$ , 0.2;  $\text{CaA}_2 + 1\text{H}_2\text{O}$ , 1.99;  $\text{SrA}_2 + 1\text{H}_2\text{O}$ , 0.88;  $\text{BaA}_2 + 1\text{H}_2\text{O}$ , 0.38;  $\text{ZnA}_2 + 6\text{H}_2\text{O}$ , 0.46;  $\text{MnA}_2 + 6\text{H}_2\text{O}$ , 0.33;  $\text{CoA}_2 + 6\text{H}_2\text{O}$ , 0.26 (*cf.* Biltz and Birk, Z. angew. Chem. 1926, 159, 125);  $\text{NiA}_2 + 6\text{H}_2\text{O}$ , 0.36;  $\text{FeA}_2 + 6\text{H}_2\text{O}$ , 0.24;  $\text{CdA}_2 + 6\text{H}_2\text{O}$ , 0.87;  $\text{CuA}_2 + 6\text{H}_2\text{O}$ , 1.05;  $\text{PbA}_2 + \text{H}_2\text{O}$ , 0.54;  $\text{AgA}_2$  anhyd. 1.72.

Naphthalene- $\beta$ -sulphonic acid forms molecular compounds with amino-acids, *e.g.*, with glycine and sarcosine (Pfeiffer *et al.*, J. pr. Chem. 1930, [ii], 126, 125) with *L*-leucine, *L*-histidine, etc. (Bermann and Stein, J. Biol. Chem. 1939, 129, 609).

**Reactions and Uses.**—Naphthalene- $\beta$ -sulphonic acid as sulphonic acid reaction mass is an essential stage in the preparation of *naphthalene-1:6-*, *2:6-*, and *2:7-disulphonic acids* and *naphthalene-1:3:6-trisulphonic acid* and the products derived therefrom. The main use for the isolated product is in the preparation of  *$\beta$ -naphthol* by fusion with caustic soda. By re-



action with aliphatic alcohols (propyl or butyl) or with formaldehyde, technically valuable "wetting-out" agents are obtained.

By nitration, a mixture of  $\alpha$ -nitronaphthalene-6- and -7-sulphonic acids is obtained, leading by reduction to the important Cleve acids. By bromination at  $0^\circ$ ,  $\alpha$ -bromonaphthalene-6- and -7-sulphonic acids are obtained in substantially equal proportion (Salkind and Belikova, J. Gen. Chem. Russ. 1934, 4, 1211; A. 1935, 612).

#### NAPHTHALENEDISULPHONIC ACIDS.

The naphthalenedisulphonic acids given in the diagram on p. 281 are manufactured by sulphonating under conditions chosen to lead to the most favourable proportion of the desired isomer. Sulphonation may be supposed to proceed with primary formation of 1:5-disulphonic acid, from 1-sulphonic acid, and of 1:6-disulphonic acid either from 2-sulphonic acid or by isomeric change of 1:5-; finally 1:5- and 1:6- are converted into 2:7- and 2:6-, the last two being inter-convertible. Chlorsulphonic acid, as was first shown by Armstrong, converts naphthalene into the 1:5-disulphonic acid; actually the 1:5-disulphenyl chloride is formed (I.G., G.P. 466441; Corbellini, Giorn. Chem. Ind. appl. 1927, 9, 118).

During the period 1920-1930 several workers studied the reactions leading to the above disulphonic acids. Fierz-David and Hasler (Helv. Chim. Acta, 1923, 6, 1133; Fierz-David, J.S.C.I. 1923, 42, 442t) treated naphthalene in sulphuric acid with just enough sulphuric anhydride to cause disulphonation and studied the changes as the temperature was raised. Below  $40^\circ$  a mixture is obtained containing 75% of 1:5- and 1:6-disulphonic acid. At temperatures between  $120^\circ$  and  $135^\circ$  the 1:5- disappears gradually and 2:7- is formed in its place, no 2:6- being yet formed. At  $140^\circ$ , however, when all 1:5- has disappeared, the 2:6-acid appears. At  $165^\circ$  there is always formed, in round numbers, a mixture containing 24% of 2:6-, 10% of 1:6-, and 65% of 2:7-disulphonic acid. The inter-conversion of the 1:6-, 2:7-, and 2:6- acids was established. The work of Ambler and Scanlan (Ind. Eng. Chem. 1927, 19, 417) and Lynch and Scanlan (*ibid.*, p. 1010) points clearly to the conclusion that the interconversion is brought about, as is the change of  $\alpha$ - to  $\beta$ -monosulphonic acid, by hydrolysis and resulphonation. When the 1:5- and 1:6-acids were heated with varying strengths of sulphuric acid (1-85%) at temperatures between  $100^\circ$  and  $220^\circ$  it was found (a) if the conditions were too mild to cause sulphonation of naphthalene, only hydrolysis to naphthalene occurred and no isomerisation; (b) under sulphonating conditions the isomeric disulphonic acids were formed in the same proportions as by sulphonating naphthalene. Heid (J. Amer. Chem. Soc. 1927, 49, 844), heated the 2:7-acid with 95% sulphuric acid at  $160^\circ$  and found gradual conversion into 2:6-acid, reaching a maximum of 42% in 19 hours, a figure higher than that given by Fierz-David for the 2:6-content of a disulphonation mixture at about this temperature.

(i) Naphthalene-1:2-disulphonic Acid.—This compound has no technical importance.

There is no evidence that it is ever formed in the sulphonation of naphthalene. It is prepared from  $\alpha$ -naphthylamine-2-sulphonic acid either by conversion into the thienaphtholsulphonic acid (Bayer, B.P. 11465, 1892; Armstrong and Wynne, Proc. C.S. 1893, 9, 168) or into the sulphinic acid (Gattermann, Ber. 1899, 32, 1156) and oxidation of these compounds by potassium permanganate.

*Identification.*—With phosphorus pentachloride a dichloride is not formed, but an anhydride (m.p.  $198^\circ$ ) results (Armstrong and Wynne, *l.c.*).

(ii) Naphthalene-1:3-disulphonic Acid is made from  $\beta$ -naphthylamine-6:8- or -5:7-disulphonic acid by boiling the corresponding hydrazine with copper sulphate solution (Armstrong and Wynne, Proc. C.S. 1890, 6, 13, 129), or from  $\alpha$ -naphthylamine-2:4-disulphonic acid by boiling the diazo-compound with alcohol (Höchst, G.P. 92082). According to Tschuk-sanova (Amer. Chem. Abstr. 1910, 34, 5834) it is formed to some extent in the sulphonation of naphthalene at  $130^\circ$ .

*Identification.*—The dichloride has m.p.  $137^\circ$  (Armstrong and Wynne, *l.c.*). The barium salt,  $\text{BaA} \cdot 4\text{H}_2\text{O}$ , potassium salt,  $\text{K}_2\text{A} \cdot 2\text{H}_2\text{O}$ , and the sodium salt are crystalline and very soluble in water.

*Reactions and Uses.*—Naphthalene-1:3-disulphonic acid is used technically in the manufacture of  $\alpha$ -naphthol-3-sulphonic acid which is prepared by fusion of the 1:3-disulphonic acid with aqueous caustic soda (B.P. 9537, 1890). Under more severe conditions of fusion, *o*-toluic acid is produced by breakdown of 1:3-dihydroxy-naphthalene with elimination of acetic acid (Kalle, G.P. 79028; Friedlander and Rüdert, Ber. 1896, 29, 1611).

(iii) Naphthalene-1:1-disulphonic Acid is of no technical importance. It is prepared from  $\alpha$ -naphthylamine-4-sulphonic acid by similar reactions to those used for the preparation of naphthalene-1:2-disulphonic acid (cf. Bayer, B.P. 26139, 1896).

*Identification.*—The dichloride has m.p.  $160^\circ$  (Armstrong and Wynne, Proc. C.S. 1893, 9, 198).

*Reaction.*—By nitration it is converted into  $\alpha$ -nitronaphthalene-5:8-disulphonic acid.

(iv) Naphthalene-1:5-disulphonic Acid (*Armstrong's acid*).—This is technically the most important disulphonic acid of naphthalene. It is formed along with the 1:6-isomer by the interaction of naphthalene in the cold with 5 parts by weight of 23% oleum (Aktienges., B.P. 4625, 1888) or with 4 parts by weight of 30% oleum. By dilution of the sulphonation mass with 3-4 parts of water the naphthalene-1:5-disulphonic acid separates as a crystalline product in technically pure form. Alternatively, by addition of salt to the diluted sulphonation mass the product is isolated as the disodium salt (Ewer and Pick, G.P.a. 2619). Sulphonation of naphthalene with chlorsulphonic acid leads to formation of naphthalene-1:5-disulphenyl chloride, 4 mol. being necessary for quantitative reaction (I.G., G.P. 466441; cf. Corbellini, Giorn. Chem. Ind. appl. 1927, 9, 118).

Fierz-David and Hasler (Helv. Chim. Acta,

1923, 6, 1135) describe the preparation and isolation of the free acid in pure form. Naphthalene (128 g.) is added to monohydrate (300 g.) and 300 g. of 64% oleum added gradually, the temperature being allowed to rise to 30° and finally raised and maintained 8 hours at 40°C. The diluted sulphonation mass is partially neutralised with sodium carbonate and then excess of sulphuric acid removed by barium carbonate. The filtered solution of the sodium salt, by concentration, acidification with hydrochloric acid, and addition of barium chloride, gives the pure barium salt of naphthalene-1:5-disulphonic acid which after filtration and conversion to the free acid by sulphuric acid is concentrated to crystallising point and 2 vols. of 38% hydrochloric acid added.

**Identification.**—The *chloride* has m.p. 183° (Armstrong, Ber. 1882, 15, 205); the *amide* melts above 310° and the *anilide* at 248–249° (Fierz-David, J.S.C.I. 1923, 42, 426*r*). The acid,  $H_2A + 4H_2O$ , crystallises in monoclinic tablets and loses  $2H_2O$  when dried in vacuum and the remainder when dried at 125°; the product dissolves in an equal weight of water at 20°. The following salts and the parts of water to dissolve 1 part of the salt at 18° are described by Fierz-David (*l.c.*):  $Na_2A + 2H_2O$ , 9 parts;  $K_2A + 2H_2O$ , 15 parts;  $CaA + 2H_2O$ , 40 parts;  $SrA + H_2O$ , 96 parts;  $BaA + H_2O$ , 470 parts;  $MgA + 6H_2O$ , 22 parts;  $ZnA + 6H_2O$ , 28 parts;  $CoA + 6H_2O$ , 46 parts;  $NiA + 6H_2O$ , 73 parts;  $CuA + 6H_2O$ , 21 parts;  $PbA + 3H_2O$ , 82 parts. According to Ewer and Pick (G.P. 41934) the lead, barium, and calcium salts are easily soluble in water but when dehydrated dissolve only very slowly.

The *benzyl-ψ-thiocarbamide* salt of naphthalene-1:5-disulphonic acid crystallises in flat tabular form, m.p. 244–245° (decomposition) and has solubility in g. per litre of 0.2*N*-hydrochloric acid 0.16/20° and 77.6/100° (Chambers and Scherer, Ind. Eng. Chem. 1924, 16, 1272).

**Reactions and Uses.**—Fusion with caustic soda according to the severity of the conditions leads to the technically important products, *α-naphthol-5-sulphonic acid* and *1:5-dihydroxynaphthalene*. By further sulphonation and nitration, followed by reduction the technically important *α-naphthylamine-4:6:8-trisulphonic acid* is produced. Nitration of the sulphonation reaction mass is the technical route to *α-nitronaphthalene-4:8-disulphonic acid* and *β-nitronaphthalene-4:8-disulphonic acid*, there being simultaneous production of *α-nitronaphthalene-3:8-disulphonic acid* from the naphthalene-1:6-disulphonic acid contained in the sulphonation mass.

Naphthalene-1:5-disulphonic acid is also an important product in the preparation of stabilised diazo-compounds (*v. DIAZO-COMPOUNDS*, Vol. III, 589*b*; *DYE STUFFS*, Azo; Vol. IV, 231*c*).

(v) **Naphthalene-1:6-disulphonic Acid.**—This acid is always formed, though in the smaller proportion, when naphthalene-1:5-disulphonic acid is made. To obtain the product in larger proportion, it is necessary to start either from isolated sodium naphthalene-β-sulphonate (Ewer and Pick, G.P. 45229) or from a β-monosulphona-

tion mass from naphthalene. Thus, Fierz-David and Hasler (Helv. Chim. Acta, 1923, 6, 1135) prepared sodium naphthalene-1:6-disulphonate by first sulphonating naphthalene (128 g.) with monohydrate (200 g.) at 165° for half an hour, cooling to 30° and completing the disulphonation by adding 275 g. 10% oleum and heating for 9 hours at 40°. The diluted reaction mass, neutralised with barium carbonate, gave the sparingly soluble barium naphthalene-1:5-disulphonate as a precipitate, along with barium sulphate, and from the filtered solution containing barium naphthalene-1:6-disulphonate the sodium salt was obtained by addition of sodium carbonate, and concentration of the filtered solution. The yield was 40–45% of theory. If naphthalene-β-sulphonic acid is used as starting material the yield is 55–60% of theory.

Arylamine salts are ineffective for the separation of the naphthalene-1:5- and 1:6-disulphonic acid but may be used for their characterisation. The *α-naphthylamine* salt of the 1:6-isomer has m.p. 272° while that of the 1:5-isomer has m.p. 231° (Forster and Hishiyama, J.S.C.I. 1932, 51, 298*r*).

**Identification.**—The *chloride* has m.p. 129° (Armstrong and Wynne, Proc. C.S. 1886, 2, 232; 1888, 4, 106) and is convertible to 1:6-*dichloronaphthalene*. The *amide* has m.p. 297–298°. The acid,  $H_2A + 4H_2O$ , crystallises in monoclinic prisms, which, in contrast to the 1:5-isomer, loses water not in stages but gradually, either under vacuum or when heated at ordinary pressure, finally melting at 125° with decomposition. The following solubilities in parts of water at 18° to dissolve 1 part of product have been determined: Acid,  $H_2A + 4H_2O$ , 0.61 parts;  $Na_2A + 6H_2O$ , 3 parts;  $K_2A$  anhydrous, 5 parts;  $(NH_4)_2A + 2H_2O$ , 2 parts;  $CaA + 4H_2O$ , 10 parts;  $SrA + 5H_2O$ , 10 parts;  $BaA + 3.5H_2O$ , 16 parts at 100°;  $ZnA + 6H_2O$ , 3 parts;  $CoA + 6H_2O$ , 5 parts;  $NiA + 6H_2O$ , 5 parts;  $CuA + 4H_2O$ , 2 parts;  $PbA + 4H_2O$ , 12 parts (Fierz-David, J.S.C.I. 1923, 42, 426*r*).

**Reactions and Uses.**—The only technical importance of naphthalene-1:6-disulphonic acid is that on nitration it produces mainly *α-nitronaphthalene-3:8-disulphonic acid* which by reduction gives the important *α-naphthylamine-3:8-disulphonic acid*. This is the desirable route if the requirement of the latter is in excess of that recovered from nitration of the naphthalene-1:5-disulphonation product (*see supra*). Sulphonation leads to *naphthalene-1:3:6-trisulphonic acid* and fusion with caustic soda gives 1:6-*dihydroxynaphthalene*.

(vi) **Naphthalene-1:7-disulphonic Acid** is of no technical importance. For its formation, see footnote, p. 280*d*. It can be prepared from *α-naphthylamine-4:6-disulphonic acid* by boiling the corresponding hydrazine with copper sulphate solution (Armstrong and Wynne, Proc. C.S. 1890, 6, 126).

**Identification.**—The *chloride* has m.p. 122.5° and is convertible into 1:7-*dichloronaphthalene* (Armstrong and Wynne, *l.c.*).

(vii) **Naphthalene-1:8-disulphonic Acid** is of no technical importance. It has been prepared from *α-naphthylamine-8-sulphonic acid* by oxidation of the corresponding thionaphthol-

sulphonic acid with permanganate (Bayer, B.P. 11465, 1892; Armstrong and Wynne, Proc. C.S. 1893, 9, 168).

**Identification.**—With phosphorus pentachloride it forms an *anhydride*, m.p. 227°. The *potassium* salt,  $K_2A + H_2O$  forms sparingly soluble, four-sided scales.

(viii) Naphthalene-2:6-disulphonic Acid is formed in the smaller proportion in the preparation of naphthalene-2:7-disulphonic acid and its preparation and isolation are described under the latter. There is no method known by which the proportion of the 2:6-isomer can be substantially altered.

**Identification.**—The *chloride* has m.p. 228–229°; the solubility of the *lead* salt is 0.19 g. per 100 c.c. water at 25° (Haller and Lynch, Ind. Eng. Chem. 1924, 16, 273). The *barium* salt is sparingly soluble. The *calcium* and *potassium* salts dissolve in 16 and 19 parts water, respectively, at 18°, and the *sodium* salt in 8.4 parts (Ebert and Merz, Ber. 1876, 9, 598). The *benzyl-ψ-thiocarbamide* salt has m.p. 200° (decomp.) (Chambers and Scherer, Ind. Eng. Chem. 1924, 16, 1272).

**Reactions and Uses.**—Naphthalene-2:6-disulphonic acid has little technical use. By fusion with caustic soda according to the severity of conditions there is produced *β-naphthol-6-sulphonic acid* (usually made by sulphonating *β-naphthol*) or 2:6-*dihydroxynaphthalene*. On nitration, *α-nitronaphthalene-3:7-disulphonic acid* is formed and on sulphonation *naphthalene-1:3:7-trisulphonic acid*.

(ix) Naphthalene-2:7-disulphonic Acid is obtained along with the 2:6-isomer and a smaller amount of 1:6-isomer by high-temperature sulphonation of naphthalene. Fierz-David and Hasler (Helv. Chim. Acta, 1923, 6, 1135), by sulphonating naphthalene (128 g.) at 165° by addition of 20 g. of 100% sulphuric acid followed by an additional 400 g. of sulphuric acid and heating 8 hours at 180°, found that there was formed a 65% yield of 2:7-isomer, 25% of 2:6-isomer, and 10% of 1:6-isomer. The presence of the 1:6-isomer in this type of sulphonation was first noted by Armstrong (Ber. 1882, 15, 204). The original work on naphthalene-2:7-disulphonic acid was by Ebert and Merz (*loc.*) and their conclusion that on prolonged heating the 2:7-isomer is converted to the 2:6-isomer has been confirmed (*see* p. 283b). A typical process for the sulphonation is described by Simpson and Olsen (Ind. Eng. Chem. 1937, 29, 1350). To 800 lb. of naphthalene heated at 150–160° is added 3,600 lb. 98% sulphuric acid during 2 hours and the mass finally maintained at 160° for 3 hours. The method of separation employed was based on the sparing solubility of the calcium salt of the 2:6-isomer in salt solution. The yield of 2:7-isomer is 50% theory and of 2:6-isomer 35% theory. This method of separation was first described in G.P. 48053 (Grünau, Landshoff, and Meyer) and depends on the fact that the calcium salt of the 2:6-isomer is practically insoluble in hot or cold salt solution, the calcium salt of the 2:7-isomer is moderately soluble in hot but sparingly soluble in cold salt solution and the small amount of calcium salt of the 1:6-isomer remains dissolved in cold salt

solution. An earlier method of separating the 2:6-isomer depended on dehydration of the calcium salts at 200–230° when the 2:6-isomer becomes very sparingly soluble (Freund, B.P. 1069, 1883).

Another method of sulphonation in which sodium naphthalene-β-sulphonate is heated with sulphuric acid at 180° has been described by Baum (G.P. 61730).

The vapour-phase sulphonation of naphthalene is said to produce mainly the 2:7-isomer. Naphthalene vapour ascends a tower heated at 220–230°, down which trickles sulphuric acid, and because of the rapid reaction and subjection of the reaction product to heat for only a brief period transformation of the 2:7-isomer to 2:6-isomer is impeded. The yield of 2:7-isomer is 75–85% (Gibbs, Ambler, and the Selden Co., B.P. 131970; Ambler, Lynch, and Haller, Ind. Eng. Chem. 1924, 16, 1264).

**Identification.**—According to Haller and Lynch (*ibid.* 1924, 16, 273) the *chloride* has m.p. 158.5–159.5°. The acid, which is very soluble in water, crystallises in long deliquescent needles. The salts of naphthalene-2:7-disulphonic acid are more soluble than the corresponding salts of the 2:6-isomer; Ebert and Merz (Ber. 1876, 9, 595) give the following composition of the salts of both isomers and the amount of water to dissolve 1 part of anhydrous salt at 18°.

2:7-Isomer.		2:6-Isomer.	
PbA, 2H <sub>2</sub> O	easily soluble.	PbA, H <sub>2</sub> O	sparingly soluble.
BaA, 2H <sub>2</sub> O	82.2 parts.	BaA, H <sub>2</sub> O	" "
CaA, 6H <sub>2</sub> O	0.2 "	CaA	16.2 parts.
K <sub>2</sub> A, 2H <sub>2</sub> O	1.4 "	K <sub>2</sub> A	10.2 "
Na <sub>2</sub> A, 6H <sub>2</sub> O	2.2 "	Na <sub>2</sub> A, H <sub>2</sub> O	8.4 "

The *benzyl-ψ-thiocarbamide* salt of naphthalene-2:7-disulphonic acid has solubility in g. per litre of 0.5x. hydrochloric acid 2.2/20° and 177.8/100° (Chamber and Scherer, Ind. Eng. Chem. 1924, 16, 1272) and m.p. 205° (decomp.) (Chambers and Watt, J. Org. Chem. 1941, 6, 376).

**Reactions and Uses.**—By sulphonation there is formed *naphthalene-1:3:6-trisulphonic acid*. By fusion with caustic soda there is formed, according to the strength of caustic soda and temperature of fusion, first *β-naphthol-7-sulphonic acid* (F-acid) and then 2:7-*dihydroxynaphthalene*. Nitration furnishes 1:8-*dinitronaphthalene-3:6-disulphonic acid*.

The main technical uses of naphthalene-2:7-disulphonic acid are for the production of *β-naphthol-7-sulphonic acid* and as intermediate for the production of Lissamine Green V (I.C.I.) (Erio Green B, Geigy) by condensation with tetraethyldiaminobenzhydrol.

#### NAPHTHALENETRISULPHONIC ACIDS.

The technically most important naphthalene-trisulphonic acid is the 1:3:6-isomer which as the sodium salt has technical applications, but its main use is in non-isolated form as the intermediate stage to H-acid by nitration, reduction and fusion with caustic soda. The only other technically valuable trisulphonic acid is the 1:3:5-isomer which in the non-isolated form is nitrated and reduced to give *α-naphthylamine-4:6:8-trisulphonic acid*, an important intermediate in the manufacture of the medicinal

product Bayer-205 ("Antrypol," I.C.I.); also by fusion with caustic soda it furnishes K-acid (1:8-aminonaphthol-4:6-disulphonic acid).

According to Gürke and Rudolph, a naphthalenetrisulphonic acid is obtained by the sulphonation of naphthalene either with 8 times its weight of 24% anhydro-acid at 180°, or with 6 times its weight of 40% anhydro-acid at 80–100°; also by the sulphonation of naphthalene-mono- and di-sulphonic acids and their salts with a proportionately smaller quantity of anhydro-acid (G.P. 38281; B.P. 15716, 1885): Two acids, at least, are obtained by these processes, the 1:3:5-trisulphonic acid, which is the chief product at the lower temperature, as Erdmann states (Ber. 1899, 32, 3188), being replaced by the 1:3:6-trisulphonic acid, the final trisulphonation product at the higher temperature (cf. Fierz and Schmid, Helv. Chim. Acta, 1921, 4, 381). As a third acid, the 1:3:7-derivative, can be obtained by the sulphonation of naphthalene-2:6-disulphonic acid, its presence in the mixture, although not recorded, is at least probable.

The naphthalenetrisulphonic acids in which two of the three sulphonic groups are relatively in the *meta*-position yield hydroxytoluic acids by digestion with caustic soda solution at 250° (Kalle, G.P. 91201), and brown dyes, possibly derived from them, by digestion with sodium sulphide, and water at 240° (Kalle, G.P. 98439).

(i) Naphthalene-1:3:5-trisulphonic Acid is formed when sodium naphthalene-1:5-disulphonate (2 parts) is heated either with monohydrate (3 parts) during 1 hour at 50°, 67% anhydro-acid (2.8 parts) being then added gradually during a second hour at this temperature, and the mixture afterwards heated at 90° during a further 3 hours, or until disulphonate is no longer precipitated from a sample by brine (Kalle, G.P.a. 11104; B.P. 1641, 1894; Erdmann, Ber. 1899, 32, 3188), or with 20% anhydro-acid (6 parts), the temperature being gradually raised to 130° and maintained at this point until sulphonation as tested by brine is complete (Fischesser, G.P.a. 7059; Bayer, G.P.a. 7004; B.P. 17141c, 1893). It is also formed by oxidising with permanganate the thionaphthol or the sulphinic acid obtained from  $\beta$ -naphthylamine-4:8-disulphonic acid (Bayer, G.P. 70296; B.P. 11465, 1892; Gattermann, Ber. 1899, 32, 1159).

**Identification.**—The acid is very soluble in water, and its behaviour recalls that of the strongest non-volatile mineral acids; the sodium salt,  $\text{Na}_3\text{A} + 4\text{H}_2\text{O}$ , forms needles very soluble in water, but only sparingly so in dilute alcohol. The chloride, rhombic prisms, m.p. 146° (Fischesser, l.c.; Gattermann, l.c.) is convertible into 1:3:5-trichloronaphthalene (Kalle, l.c.; G.P. 82563).

**Reactions and Uses.**—On sulphonation it yields naphthalene-1:3:5:7-tetrasulphonic acid. Fusion with caustic alkali converts it into  $\alpha$ -naphthol-3:5-disulphonic acid and 1:5-dihydroxynaphthalene-3-sulphonic acid, but digestion with strong caustic soda solution at 250° gives *o*-hydroxy-*o*-toluic acid (Kalle, G.P. 91021; B.P. 16559, 1894). Nitration furnishes  $\alpha$ -nitronaphthalene-4:6:8-trisulphonic acid from which by reduction

is obtained the technically important  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid.

(ii) Naphthalene-1:3:6-trisulphonic Acid is obtained when sodium naphthalene-1:6- or 2:7-disulphonate is heated with twice its weight of 24% anhydro-acid, the temperature being raised gradually to 180° (cf. Gürke and Rudolph, G.P. 38281; B.P. 15716, 1885; Bayer, G.P. 63015), or, mixed with 1:3:5-trisulphonic acid, when naphthalene or sodium naphthalene- $\beta$ -sulphonate is heated with 40% anhydro-acid at 150–160° (Gürke and Rudolph, l.c.) and when naphthalene is heated with 3–5.4 times its weight of chlorosulphonic acid at 150° for an hour (Armstrong and Wynne, Proc. C.S. 1887, 3, 146). It is formed also by eliminating the amino-group either from  $\beta$ -naphthylamine-2:4:7-trisulphonic acid (Armstrong and Wynne, *ibid.* 1890, 6, 125) or from  $\beta$ -naphthylamine-3:6:8-trisulphonic acid (Dressel and Kothe, Ber. 1894, 27, 2154).

**Preparation.**—Monohydrate (380 parts) is added very slowly to naphthalene (256 parts) at 165°, the melt kept at this temperature for an hour, then cooled to 75°, diluted with monohydrate (120 parts) cooled to 50°, and mixed cautiously with 60% anhydro-acid (900 parts), stirring being continuous, and finally heated at 165° for 6 hours to ensure complete conversion of mono- into tri-sulphonic acid, which without being isolated is then available for nitration. The yield of 1:3:6-trisulphonic acid may amount to 60% of that calculated (H. E. Fierz-David, "Dye Chemistry," Churchill, 1921, p. 12).

**Identification.**—The sodium salt  $\text{Na}_2\text{A} + 5\text{H}_2\text{O}$  forms very soluble needles and the chloride small prisms, m.p. 194° (Armstrong and Wynne, l.c.; Dressel and Kothe, l.c.).

**Reactions and Uses.**—By fusion with 50% caustic soda solution at 170–180° there is produced  $\alpha$ -naphthol-3:6-disulphonic acid (Violet acid) and with 90% caustic soda at 250° 1:6-dihydroxynaphthalene-3-sulphonic acid. By nitration there is formed  $\alpha$ -nitronaphthalene-3:6:8-trisulphonic acid which by reduction gives  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid (Koch acid) and this on fusion with caustic soda gives H-acid. The total reaction product of the sulphonation of naphthalene to trisulphonic acid in the form of its sodium salt finds some application as a stabiliser for diazo-solutions ("Azoguard"). Sodium naphthalene-1:3:6-trisulphonate, particularly as the total crude reaction product, has a solubilising effect on other products. Thus, Korolev, Bilik, and Tscheksanova (B. 1936, 440) state that salts of naphthalene-1:3:6-trisulphonic acid yield colloidal solutions in water and act as protective colloids, for example, retarding or preventing the precipitation of the benzidine salts of naphthalene-2:6- and 2:7-disulphonic acids.

(iii) Naphthalene-1:3:7-trisulphonic Acid is obtained when sodium naphthalene-2:6-disulphonate (1 part) dissolved in monohydrate (3 parts), is heated with 60% anhydro-acid (1 part) on a water bath until a test, on addition of common salt, gives no separation of the disulphonate (Cassella, G.P. 75432). It is also formed by oxidising with permanganate the thionaphthols from  $\alpha$ -naphthylamine-3:7-disul-

phonic acid and  $\beta$ -naphthylamine-6:8-disulphonic acid (Bayer, G.P. 70296; B.P. 11465, 1892), and by eliminating the amino-group from  $\beta$ -naphthylamine-3:5:7-trisulphonic acid (Dressel and Kothe, Ber. 1894, 27, 1203).

*Identification*.—The *chloride* forms large prisms, m.p. 165–166° (Dressel and Kothe, l.c.).

*Reactions*.—On sulphonation it yields *naphthalene-1:3:5:7-tetrasulphonic acid*. Digestion with 50% caustic soda solution at 260° converts it into *p-hydroxy-o-toluic acid* (Kalle, G.P. 91201; B.P. 16559, 1894). Nitration furnishes *a-nitro-naphthalene-3:5:7-trisulphonic acid*.

(iv) *Naphthalene-1:4:8-trisulphonic Acid* is obtained by oxidising with permanganate the thionaphthol or the sulphinic acid prepared from  $\alpha$ -naphthylamine-4:8-disulphonic acid (Bayer, G.P. 70296; B.P. 11465, 1892; Gattermann, Ber. 1899, 32, 1156).

*Identification*.—The *chloride* forms clusters of needles, m.p. 156–157° (Gattermann, l.c.).

(v) *Naphthalene-2:3:6-trisulphonic Acid*, obtained by oxidising with permanganate the thionaphthol from  $\beta$ -naphthylamine-3:6-disulphonic acid (Bayer, l.c.; Armstrong and Wynne, Proc. C.S. 1893, 9, 168), is also the product formed by eliminating the amino-group from  $\beta$ -naphthylamine-3:6:7-trisulphonic acid (Dressel and Kothe, Ber. 1894, 27, 1202).

*Identification*.—The *potassium salt* ( $+5\text{H}_2\text{O}$ ) is microcrystalline; the *chloride* forms flat prisms, m.p. 200° (Armstrong and Wynne, l.c.).

The following acids:

- (vi) *Naphthalene-1:2:5-trisulphonic acid*,
- (vii) *Naphthalene-1:2:6-trisulphonic acid*,
- (viii) *Naphthalene-1:3:8-trisulphonic acid*,
- (ix) *Naphthalene-1:4:7-trisulphonic acid*,

obtained, like the 2:3:6-trisulphonic acid, from the corresponding thio- $\alpha$ - or  $\beta$ -naphtholdisulphonic acids by oxidation, form sodium salts which are very soluble in water (Bayer, l.c.), but have not been further described.

#### NAPHTHALENETETRASULPHONIC ACIDS.

The naphthalenetetrasulphonic acids have no technical importance. Each of the two methods employed for the tetrasulphonation of naphthalene has been stated to furnish more than one tetrasulphonic acid. Senhofer (Monatsh. 1882, 3, 111), by using a mixture of sulphuric acid with phosphoric oxide at 260° for 3–4 hours obtained a product which by fractional crystallisation of the mixed barium or copper salt furnished an acid now identified by Fierz and Schmid as the 1:3:5:7-tetrasulphonic acid (Helv. Chim. Acta, 1921, 4, 381). With 40% anhydro-acid at 160° for 9 hours, or with chlorosulphonic acid (Bayer, G.P. 40893), at least two tetrasulphonic acids were said to be formed, and to avoid the production of isomers, the 2:6-disulphonic acid replaced naphthalene in later developments of the process (Bayer, G.P. 79054; 80464; B.P. 25074, 1893; cf., however, G.P. 89242), furnishing, like the 1:3:7-trisulphonic acid under similar conditions, a tetrasulphonic acid, the *chloride* of which melted at 261–262° (Bayer, G.P.a. 7224; B.P. l.c.).

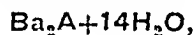
On reinvestigating the subject, Fierz and

Schmid (l.c.) have reached the following conclusions:

1. That energetic sulphonation with anhydro-acid converts naphthalene into a mixture of the 1:3:6-trisulphonic and the 1:3:5:7-tetrasulphonic acids;
2. That the 1:3:5:7-derivative is the only tetrasulphonic acid arising from the sulphonation of naphthalene;
3. That this tetrasulphonic acid is formed very readily in the melt, but independently of the 1:3:6-trisulphonic acid unless, by the use of only weakly fuming sulphuric acid, isomerisation occurs followed by further sulphonation. They further suggest that the simultaneous formation of the tri- and tetra-sulphonic acids accounts to a large extent for the apparent loss of material in the production of H-acid from the trisulphonation melt, in which only the trisulphonic acid can be nitrated.

(i) *Naphthalene-1:3:5:7-tetrasulphonic Acid* is obtained when calcium naphthalene-2:6-disulphonate, dried at 200°, is heated with 3 times its weight of 25% anhydro-acid at 90° during 4 hours and then at 260° during 6 hours. The product is converted into sodium salt, which can be separated from a hot concentrated solution by common salt as a heavy sand-like precipitate (Bayer, G.P. 79054; B.P. 25074, 1893).

*Identification*.—The *barium salt*,



is efflorescent, that with  $8\text{H}_2\text{O}$  is stable in the air (Fierz and Schmid, l.c.). The *chloride* forms very sparingly soluble, compact, cubical crystals, m.p. 261–262° (Bayer, G.P.a. 7224; Fierz and Schmid, l.c.).

*Reactions*.—Fusion with caustic alkali converts it into 1:3:5-trihydroxynaphthalene-7-sulphonic acid, but digestion with 15% caustic soda solution furnishes *a-naphthol-3:5:7-trisulphonic acid* and with 60% solution a mixture of the isomeric 1:3-dihydroxynaphthalene-5:7- and 1:5-dihydroxynaphthalene-3:7-disulphonic acids. It cannot be nitrated.

(ii) *Naphthalene-1:3:6:7-tetrasulphonic Acid* has been prepared by oxidising with permanganate the thionaphthol obtained from  $\beta$ -naphthylamine-3:6:8-trisulphonic acid (Bayer, G.P. 70296; B.P. 11465, 1892).

*Identification*.—The *sodium salt* forms a very soluble granular mass. The *chloride* crystallises in needles, m.p. 309–310°, sparingly soluble in benzene (Bayer, G.P.a. 7224).

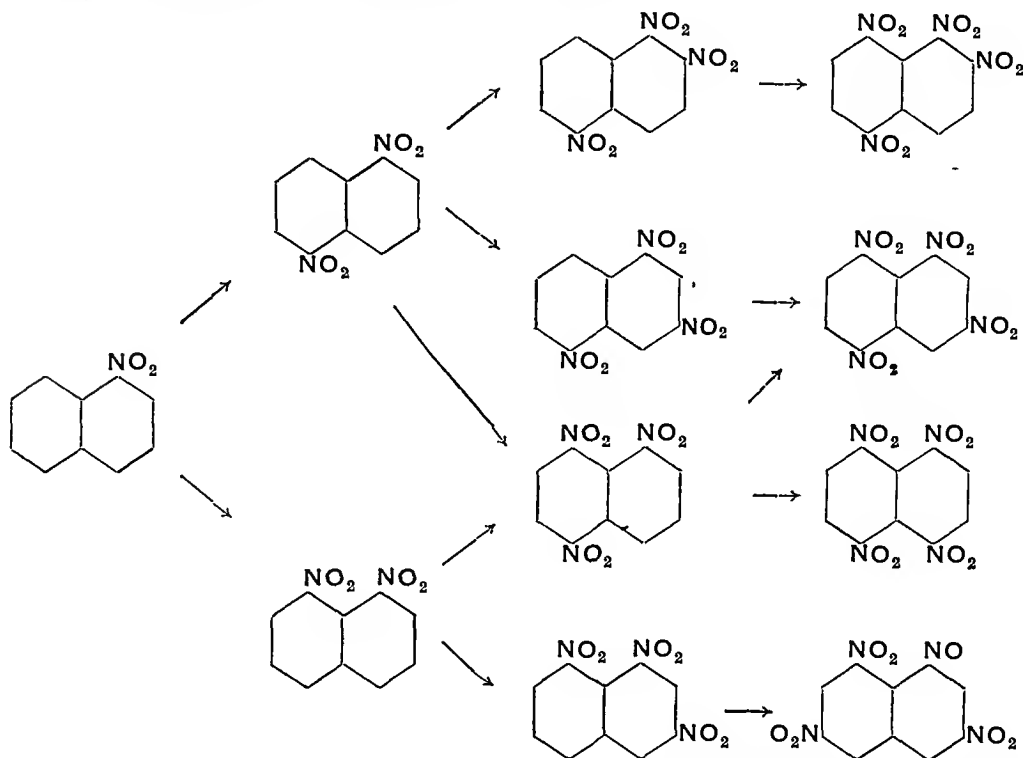
(iii) *Naphthalene-1:3:6:8-tetrasulphonic Acid* is obtained similarly from  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid.

*Identification*.—The *barium salt* is only sparingly soluble, but the crystalline *sodium salt* easily soluble in water. The *chloride*, short prisms, m.p. 282–283°, dissolves only very sparingly in benzene, but more readily in acetone (Bayer, l.c.).

## NITRONAPHTHALENES.

The action of nitric acid on naphthalene was first studied by Laurent who described  $\alpha$ -nitronaphthalene under the name nitronaphthalase (Ann. Chim. Phys. 1835, [ii], 59, 376; cf. Lautemann and Aguiar, Bull. Soc. chim., 1865, [ii], 3, 261). The first product of nitration is  $\alpha$ -

nitronaphthalene, accompanied by a small proportion of  $\beta$ -nitronaphthalene (*see later*) and dinitronaphthalenes. Dinitration gives 1:5- and 1:8-dinitronaphthalene, and the further nitration products, neglecting any arising from  $\beta$ -nitronaphthalene, are shown in the following scheme:



It will be noted that, unlike sulphonic groups, two nitro-groups can take up 1:2-, 1:4-, and 1:8-positions in the naphthalene ring. Nitration resembles sulphonation in that the di-substitution products are wholly heteronuclear.

By reduction, usually with iron and dilute sulphuric acid, the nitronaphthalenesulphonic acids are converted into the corresponding naphthylaminesulphonic acids, which in not a few cases are of technical importance, being isomeric with those obtained from the naphthylamines by sulphonation.

Unlike nitrated hydrocarbons of the benzene series, the nitronaphthalenes are of little importance as explosives. Crude tetranitronaphthalene, for example, obtained by heating crude dinitronaphthalene with 15 times its weight of a mixture containing 30% of nitric acid ( $\rho$  1.5) and 70% of sulphuric acid at a temperature not exceeding 130° for an hour, is almost insensitive to detonation and percussion, and when heated burns quietly with a smoky flame without explosion (Escales, Nitrosprengstoffe, ed. 1915, 168, 331). Dinitronaphthalene, (mixture of 1:5- and 1:8- isomers) is used to some extent in blasting explosives (*see* Vol. IV, 474c-475b).

## MONONITRONAPHTHALENES

$\alpha$ -Nitronaphthalene, for laboratory purposes, may be prepared by adding very finely

powdered naphthalene (128 g.) to a mixture of 60% nitric acid (103 g.) and 80% sulphuric acid (300 g.) stirring continuously for 6 hours at 50°, and completing the reaction at 60° for 1 hour. The product, boiled with water to remove acid and unchanged naphthalene, may be freed from dinitronaphthalene by extraction with carbon disulphide (*cf.* Beilstein and Kuhlberg, Annalen, 1873, 169, 81). Recently, Fierz-David and Sponagel have studied the nitration of naphthalene. They showed that the nitration product obtained as above contains about 0.4% of 2:4-dinitro- $\alpha$ -naphthol, which can be removed by aqueous caustic soda. Subsequent distillation at 12 mm. gives a mixture of mononitronaphthalenes of setting point 49-51° containing 4.6% of  $\beta$ -nitronaphthalene (yield about 94.5%), leaving a residue containing 1:5- and 1:8-dinitronaphthalenes. Pure  $\alpha$ -nitronaphthalene is obtained by several recrystallisations of the distillation product from ethyl alcohol and light petroleum. The authors give a melting-point diagram for mixture of  $\alpha$ - and  $\beta$ -isomers; the eutectic mixture contains 56% of  $\alpha$ -nitronaphthalene (Helv. Chim. Acta, 1943, 26, 98).

On the manufacturing scale, high quality naphthalene crystals are nitrated in a jacketed cast-iron pan at a temperature rising to 60°, cooling being necessary. The nitrating agent may be mixed nitric-sulphuric acid or a mixture



of sulphuric acid and sodium nitrate. Similar processes have been described by Witt (Chem. Ind. 1887, 10, 216) and Höchst (G.P. 201623). When nitration is complete the batch is allowed to separate into two layers, the lower layer of spent acid is run off, and the molten nitronaphthalene is run into hot water and well washed with water and dilute alkali. If a purer product is required it may be obtained by crystallising from solution in one-fourth of its weight of solvent naphtha (Paul, Z. angew. Chem. 1897, 10, 146) or by sweating (Du Pont, U.S.P. 1836211).

**Identification.**—Pure  $\alpha$ -nitronaphthalene crystallises in slender lustrous needles; it is odourless and has m.p.  $57.8^\circ$  (block, Fierz-David and Sponagel, l.c.; Enz and Pfister, *ibid.* 1930, 13, 194, gave  $56.5^\circ$ ). It is practically non-volatile in steam, readily soluble in benzene and its homologues, carbon disulphide, ether, and hot alcohol; 1 part dissolves in 35–36 parts of 87.5% alcohol at  $15^\circ$ . Its vapour attacks the eyes, and it is poisonous.

**Reactions.**—With chromic acid in acetic acid solution it is oxidised to 3-nitrophthalic acid (Beilstein and Kurbatow, Annalen, 1880, 202, 217); with 5% potassium permanganate to 3-nitrophthalonic acid and 3-nitrophthalic acids (Friedländer and Weisberg, Ber. 1895, 28, 1642), but with cupric or ferric oxide and caustic soda solution at  $250^\circ$  to a mixture of phthalic and benzoic acids (Bindschedler, G.P. 136410, 140999; B.P. 15527, 1901). Alkaline permanganate oxidation followed by treatment with aniline gives the aniline salt of phthalonic acid, the nitro-containing ring being attacked in this case (Gardner, J. Amer. Chem. Soc. 1927, 49, 1831). When oxidised in the vapour phase by a large excess of air in presence of vanadic oxide at  $340$ – $350^\circ$ , it gives rise to a mixture of phthalimide and phthalic anhydride (Green, J.S.C.I. 1932, 51, 147r).

When boiled with ammonium sulphite solution it is converted into a mixture of  $\alpha$ -naphthylamine-N-sulphonic and -4-sulphonic acids, but with sodium bisulphite solution into  $\alpha$ -naphthylamine-2:4-disulphonic acid mixed with a small amount of the -4-sulphonic acid. Reduction in acid solution converts it into  $\alpha$ -naphthylamine. With excess of hydrogen, in contact with finely divided copper at  $330$ – $350^\circ$ , it also gives  $\alpha$ -naphthylamine, but with nickel at this temperature not only  $\alpha$ -naphthylamine but tetrahydronaphthalene, ammonia, and naphthalene are produced (Sabatier and Senderens, Compt. rend. 1902, 135, 226). In alcoholic solution with sodium amalgam, azoxynaphthalene is formed (Jaworsky, J. pr. Chem. 1865, [i], 94, 285). For its reduction to tetrahydro- $\alpha$ -naphthylamine, see pp. 413b, 419b.

When  $\alpha$ -nitronaphthalene, dissolved in benzene or carbon tetrachloride, is chlorinated in the presence of iodine or ferric chloride, 1:5- and 1:8-chloronitronaphthalenes are obtained together with nitronaphthalene chlorides which, when heated in a vacuum, furnish naphthalene and chloro-, dichloro-, and trichloro-naphthalenes (Buffle and Cordaz, A. 1932, 1241).

$\alpha$ -Nitronaphthalene with sodamide and piperidine gives 1-nitro-4-piperidinonaphthalene, m.p.

$73.5$ – $74^\circ$ , reducible to 1-amino-4-piperidinonaphthalene, m.p.  $78$ – $79^\circ$  (Bradley and Robinson, J.C.S. 1932, 1254).

$\beta$ -Nitronaphthalene is formed in small quantity in the nitration of naphthalene but must be prepared by indirect methods.

**Preparation.**—It can be obtained from 2-nitro- $\alpha$ -naphthylamine by the diazo-reaction (Lellmann and Remy, Ber. 1886, 19, 236; Lellmann, *ibid.* 1887, 20, 891); in 7% yield from  $\beta$ -diazonaphthalene nitrite by treatment with cuprous oxide (Sandmeyer, *ibid.* 1887, 20, 1496); in 25% yield, from diazotised  $\beta$ -naphthylamine sulphate by interaction with cupro-cupric sulphite and potassium nitrite solution at the ordinary temperature (Hantzsch and Blagden, *ibid.* 1900, 33, 2554); in 30% yield from 2-nitro- $\alpha$ -naphthylamine (Hodgson and Kilner, J.C.S. 1926, 7; Hodgson, Leigh, and Turner, J.C.S. 1942, 744); and from  $\beta$ -nitrotetralin by bromination and dehydrobromination (Tetralin G.m.b.H., G.P. 332593; see also G.P. 299014; von Braun *et al.*, Ber. 1922, 55 [B], 1687).

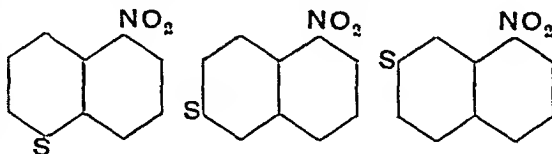
**Identification.**—It crystallises from dilute alcohol in small yellow needles, m.p.  $79^\circ$  ( $75.1^\circ$  according to Lenkhold, Anilinokras Prom. 1932, 2, 16–17), has an odour of cinnamon, and volatilises only slowly with steam.

**Reactions.**—On sulphonation, it yields a mixture of  $\beta$ -nitronaphthalene-5- and -8-sulphonic acids. When warmed with methyl alcoholic potash it gives 2-nitroso- $\alpha$ -naphthol. When nitrated in sulphuric acid solution it gives 1:3:8-trinitro-, but in glacial acetic acid solution 2:5- and 2:8-dinitro-naphthalene, melting at  $160$ – $161.5^\circ$  and  $166^\circ$  respectively (Vesely and Jakeš, Bull. Soc. chim. 1923, [iv], 33, 952). On reduction with zinc and alcohol it gives azoxy-, azo-, and hydroazo-compounds in the same way as nitrobenzene (Cumming and Steel, J.C.S. 1923, 123, 2464; Cumming and Ferrier, *ibid.* 1924, 125, 1108).

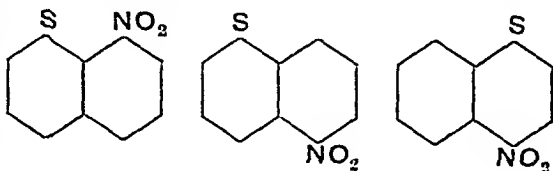
#### NITRONAPHTHALENESULPHONIC ACIDS.

The known nitronaphthalenesulphonic acids are mostly  $\alpha$ -nitro-compounds and are obtained either by sulphonation of  $\alpha$ -nitronaphthalene or by nitration of naphthalene- $\alpha$ - or - $\beta$ -monosulphonic acids. The products from each of these sources are: ( $S=SO_3H$ ).

(a) By sulphonation of  $\alpha$ -nitronaphthalene:

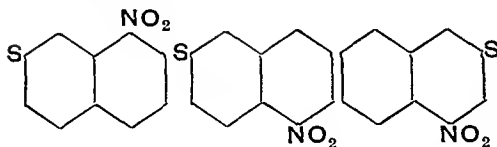


(b) By nitration of naphthalene- $\alpha$ -sulphonic acid:





(c) By nitration of naphthalene- $\beta$ -sulphonic acid:



The separation of the isomeric acids obtained by these methods is not easy, and for technical purposes is not attempted, as the naphthylamine-sulphonic acids, for the production of which they are made, can be isolated from the respective reduction products with much less difficulty.

On comparing these products of the nitration of naphthalenemonosulphonic acids with those of naphthalene-di- and -tri-sulphonic acids (see pp. 292, 293) it will be noticed that the former always, but the latter only rarely, furnish isomers; also that the nitro-group can assume the 1:4-(*para*-) or the 1:8-(*peri*-) but not the 1:2-(*ortho*-) position relatively to the sulphonic-group.

Certain nitronaphthalenesulphonic acids have shown photosensitivity, particularly the 1:8- and 1:2-isomers; some have found application in tanning agents. The nitration of naphthalene-mono-, -di-, and -tri-sulphonic acids in presence of sulphuric acid under a wide range of experimental conditions has been studied by R. Lantz (Bull. Soc. chim. 1939, [v], 6, 280).

#### Nitronaphthalenemonosulphonic Acids.

(i)  $\alpha$ -Nitronaphthalene-2-sulphonic Acid, obtainable from  $\alpha$ -naphthylamine-2-sulphonic acid by diazotisation and treatment with copper bronze or cuprous compounds, gives a *chloride*, m.p. 120.5°; *amide*, m.p. 214.3° (Voroschcov and Koslov, A. 1933, 386).

(ii)  $\alpha$ -Nitronaphthalene-3-sulphonic Acid (Cleve's [ $\gamma$ ]-nitronaphthalenesulphonic acid), formed in small amount when sodium naphthalene- $\beta$ -sulphonate is nitrated (see the 6-sulphonic acid), is obtained from the sulphonyl chloride by boiling with water (Cleve, Ber. 1886, 19, 2179; cf. Armstrong and Wynne, Proc. C.S. 1895, 11, 239).

*Identification*.—The *lead* salt,  $\text{PbA}_2 + 3\text{H}_2\text{O}$ , *barium* salt,  $\text{BaA}_2 + 3\text{H}_2\text{O}$ , and *potassium* salt,  $\text{KA}$ , crystallise in sparingly soluble needles. The *chloride* forms needles, m.p. 140°, convertible into 1:3-dichloronaphthalene. Reduction converts the acid into  $\alpha$ -naphthylamine-3-sulphonic acid (Cleve, l.c.).

(iii)  $\alpha$ -Nitronaphthalene-4-sulphonic Acid, formed in small quantity by the nitration of sodium naphthalene- $\alpha$ -sulphonate (see the 8-sulphonic acid), is isolated from the product by means of its chloride (Cleve, Ber. 1890, 23, 959).

*Identification*.—The *barium* salt,  $\text{BaA}_2 + \text{H}_2\text{O}$ , forms needles soluble in 66 parts of cold and 33 parts of boiling water; the *calcium* salt,  $\text{CaA}_2 + 2\text{H}_2\text{O}$ , scales soluble in 37 parts of water at 17° and 16 parts at 100°; the *potassium* salt,  $\text{KA}$ , needles; and the *sodium* salt,

$\text{NaA} + \text{H}_2\text{O}$ , needles. The *chloride* forms prisms, m.p. 99°. Reduction converts the acid into  $\alpha$ -naphthylamine-4-sulphonic acid (Cleve, l.c.).

(iv)  $\alpha$ -Nitronaphthalene-5-sulphonic Acid (Cleve's [ $\alpha$ ]-acid) is obtained as chief product (about 80%) when  $\alpha$ -nitronaphthalene is sulphonated with anhydro-acid; but as minor product (20–30%; see the 8-sulphonic acid) when sodium naphthalene- $\alpha$ -sulphonate is nitrated. It is said to be the only product of the interaction of  $\alpha$ -nitronaphthalene and chlorosulphonic acid (Armstrong and Williamson, Proc. C.S. 1886, 2, 233).

*Preparation*.—(1) Finely divided dry  $\alpha$ -nitronaphthalene (20 parts) is added to a mixture of sulphuric acid (35 parts) and 24% anhydro-acid (25 parts) at such a rate that the temperature does not rise above 90°, and the mixture maintained at this temperature during 8 hours or until sulphonation is complete. The product, poured on to an equal weight of ice, gives a crystalline separation of the pure 5-sulphonic acid (Witt, Chem. Ind. 1887, 10, 218). From the mother-liquor, the isomeric 6- and 7-sulphonic acids can be isolated by conversion into, and fractional crystallisation of, the nitronaphthalenesulphonyl chlorides (Palmaer, Ber. 1881, 21, 3260).

(2) The formation of dark resinous substances, unavoidable when  $\alpha$ -nitronaphthalene is sulphonated by anhydro-acid, does not occur if fused salt is added to the acid in quantity sufficient to convert the dissolved anhydride into chlorosulphonic acid. Following this modified process,  $\alpha$ -nitronaphthalene (10 parts) is added to the mixed sulphuric and chlorosulphonic acids obtained from 20% anhydro-acid (26 parts), and the mixture heated on a water-bath until sulphonation is complete (Erdmann, Annalen, 1888, 247, 315).

*Identification*.—The acid,  $\text{HA} + 4\text{H}_2\text{O}$ , crystallises in easily soluble pale yellow needles; the *lead* salt,  $\text{PbA}_2 + 3\text{H}_2\text{O}$ , in scales; and the *barium* salt,  $\text{BaA}_2 + 3\text{H}_2\text{O}$ , in sparingly soluble needles (Cleve, Bull. Soc. chim. 1875, [ii], 24, 510). The *calcium* salt,  $\text{CaA}_2 + 2\text{H}_2\text{O}$ , forms sparingly soluble needles; the *potassium* salt,  $\text{KA} + \text{H}_2\text{O}$ , hexagonal tables soluble in 25 parts of water at 17° (Erdmann, Annalen, 1893, 275, 247); the *sodium* salt,  $\text{NaA} + \frac{1}{2}\text{H}_2\text{O}$ , very soluble tables (Cleve, l.c.). The *chloride*, needles, m.p. 113°, is convertible into 1:5-dichloronaphthalene (Cleve, l.c.).

*Reactions*.—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-5-sulphonic acid; with sodium amalgam into  $\alpha$ -naphthylamine (Claus, Ber. 1877, 10, 1303); and electrolytically into 1-amino-4-naphthol-5-sulphonic acid, doubtless by transformation of the hydroxylamine first formed (cf. Fierz and Weissenbach, Helv. Chim. Acta, 1920, 3, 305). Nitration furnishes 1:8-dinitronaphthalene-5-sulphonic acid.

(v)  $\alpha$ -Nitronaphthalene-6-sulphonic Acid (Cleve's [ $\beta$ ]-acid). A mixture of this acid with about an equal quantity of the 7-sulphonic acid forms almost the entire product of the nitration of sodium naphthalene- $\beta$ -sulphonate, the 3-sulphonic acid being present only in very

small amount. A mixture of the 6- and 7-sulphonic acids constitutes the minor product of the sulphonation of  $\alpha$ -nitronaphthalene (see the 5-sulphonic acid).

**Preparation.**—(1) Sodium naphthalene- $\beta$ -sulphonate (23 parts) is stirred into sulphuric acid (115 parts) at a temperature not exceeding 30°, the whole cooled to 0°, and a mixture of nitric acid (7 parts  $\text{HNO}_3$ ) and sulphuric acid then added at 0–10°, the nitration being completed at this temperature. After removal of the excess of sulphuric acid by lime, the filtrate is used either for the isolation of the 6- and 7-sulphonic acids or for their reduction to the corresponding  $\alpha$ -naphthylaminesulphonic acids (Cassella, G.P. 67017; B.P. 6972, 1891; cf. G.P. 85058).

(2) Sodium naphthalene- $\beta$ -sulphonate is stirred into cold nitric acid,  $\rho$  1.3, the mixture warmed to complete the nitration, and the product converted into barium salt. By extraction of this salt with boiling water, the greater part of the sparingly soluble 6-sulphonate remains undissolved. To separate the remainder, the filtrate, which in addition contains the 7- and 3-isomers, is evaporated to dryness, the residue converted into chloride, and this extracted by carbon disulphide, in which the 7-sulphonyl chloride is only sparingly soluble. The 6- and 3-sulphonyl chlorides are then separated by fractional crystallisation from the solution (Cleve, Bull. Soc. chim. 1876, [ii], 26, 444; 1878, [ii], 29, 414; Ber. 1886, 19, 2179; cf. Erdmann and Süvern, Annalen, 1893, 275, 251).

**Identification.**—The acid crystallises in readily soluble brown needles; the barium salt,  $\text{BaA}_2 + \text{H}_2\text{O}$ , in needles soluble in 782 parts of water at 22°; the calcium salt,  $\text{CaA}_2 + \text{H}_2\text{O}$  in scales; the potassium salt,  $\text{KA}$ , in tables soluble in 29 parts of water at 20°; the sodium salt,  $\text{NaA} + 3\text{H}_2\text{O}$ , in crusts consisting of scales. The chloride forms prisms, m.p. 125.5°, convertible into 1:6-dichloronaphthalene (Cleve, l.c.).

**Reactions.**—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-6-sulphonic acid, and electrolytically into 1-amino-4-naphthol-6-sulphonic acid (cf. Fierz and Weissenbach, l.c.). Nitration furnishes 1:8-dinitronaphthalene-6-sulphonic acid.

(vi)  $\alpha$ -Nitronaphthalene-7-sulphonic Acid (Cleve's [8-] or [8-nitronaphthalenesulphonic acid] constitutes about one-half of the product when either sodium naphthalene- $\beta$ -sulphonate (see the 6-sulphonic acid; cf. Cassella, G.P. 85058), or naphthalene- $\beta$ -sulphonyl chloride (Erdmann and Süvern, Annalen, 1893, 275, 238) is nitrated, but is formed only in small amount when  $\alpha$ -nitronaphthalene is sulphonated (see the 5-sulphonic acid).

**Identification.**—The acid forms brown needles, very soluble in water, but, unlike the 6-sulphonic acid, is almost insoluble in concentrated hydrochloric acid, and less soluble than it is in 33% sulphuric acid. The barium salt,  $\text{BaA}_2 + 3\frac{1}{2}\text{H}_2\text{O}$ , forms granular aggregates of needles, soluble, when anhydrous, in 377 parts of water at 17° but in 9.1 parts of boiling water; the calcium salt, very soluble needles; the potassium salt,  $\text{KA} + \frac{1}{2}\text{H}_2\text{O}$ , needles readily soluble in water;

the sodium salt, spherical aggregates of needles (Palmaer, Ber. 1888, 21, 3261). The chloride forms prisms, m.p. 169°, convertible into 1:7-dichloronaphthalene (Cleve, Bull. Soc. chim. 1878, [ii], 29, 414; Armstrong and Wynne, Proc. C.S. 1889, 5, 19).

**Reactions.**—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-7-sulphonic acid, and electrolytically into 1-amino-4-naphthol-7-sulphonic acid (cf. Fierz and Weissenbach, l.c.). Nitration furnishes 1:5-dinitronaphthalene-7-sulphonic acid.

(vii)  $\alpha$ -Nitronaphthalene-8-sulphonic Acid is obtained as chief product (60–70%; see the 5-sulphonic acid) when sodium naphthalene- $\alpha$ -sulphonate is nitrated.

**Preparation.**—(1) Sodium naphthalene- $\alpha$ -sulphonate (4 parts) is stirred into nitric acid,  $\rho$  1.45 (6 parts), and the product converted into calcium salt. From the solution of the calcium salt, the greater part of the 5-sulphonate is separated by concentration, the more soluble 8-sulphonate being contained in the mother-liquors (Cleve, Ber. 1890, 23, 958). For technical purposes the separation is unnecessary, as the corresponding naphthylaminesulphonic acids differ to a much greater degree in solubility, and are more easily isolated (cf. Schöllkopf, G.P. 40571; B.P. 15775, 1885).

(2) The acid can be obtained by stirring naphthalene- $\alpha$ -sulphonyl chloride into 3 times its weight of nitric acid,  $\rho$  1.475, at  $-5^\circ$ , extracting the  $\alpha$ -nitronaphthalene-4- and -5-sulphonyl chlorides from the product by carbon disulphide, in which the 8-isomer is almost insoluble, and hydrolysing the residue (Erdmann and Süvern, Annalen, 1893, 275, 237; cf. Reissert, Ber. 1922, 55 [B], 862).

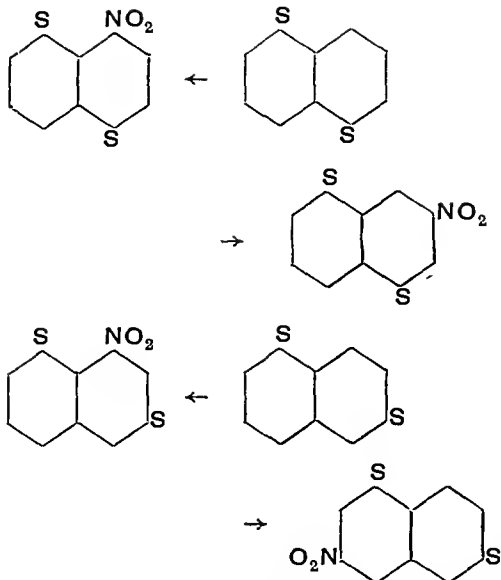
**Identification.**—The acid forms needles; the barium salt,  $\text{BaA}_2 + 2\frac{1}{2}\text{H}_2\text{O}$ , crusts; the calcium salt,  $\text{CaA}_2 + 4\frac{1}{2}\text{H}_2\text{O}$ , scales; the potassium salt,  $\text{KA} + \text{H}_2\text{O}$ , needles, or  $\text{KA} + 2\frac{1}{2}\text{H}_2\text{O}$ , scales, all easily soluble in water. The chloride forms prisms, m.p. 161° (Erdmann and Süvern, l.c.). Reduction converts the acid into  $\alpha$ -naphthylamine-8-sulphonic acid.

(viii)  $\beta$ -Nitronaphthalene-1-sulphonic Acid is formed from  $\beta$ -naphthylamine-1-sulphonic acid by a Sandmeyer reaction (Voroshnev, Koslov, and Travkin, J. Gen. Chem. Russ. 1939, 9, 522).

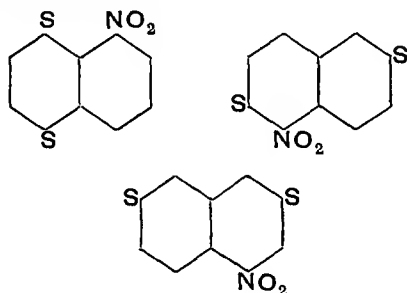
(ix and x)  $\beta$ -Nitronaphthalene-5-sulphonic Acid, mixed with the 8-sulphonic acid, is obtained by sulphonating  $\beta$ -nitronaphthalene with ice-cooled anhydro-acid, and separated from it by fractional crystallisation of the mixed chlorides from benzene. The 5-sulphonyl chloride, prisms, m.p. 127°, is more soluble in benzene than the 8-sulphonyl chloride, needles, m.p. 169–170° (Kappeler, Ber. 1912, 45, 634).

#### Nitronaphthalenedisulphonic Acids.

The nitronaphthalenedisulphonic acids are obtained for the most part from naphthalenedisulphonic acids by nitration. With two of these acids, viz. the naphthalene-1:5- and 1:6-disulphonic acids, both  $\alpha$ - and  $\beta$ -nitro-derivatives are formed, the  $\alpha$ -nitrodisulphonic acid being the chief product:



but with each of the 1:4-, 2:6-, and 2:7-disulphonic acids only one, and that the  $\alpha$ -nitro-acid, has been isolated:



According to Lantz (Bull. Soc. chim. 1939, [v], 6, 280-289) the total number of substituents ( $\text{SO}_3\text{H}$  and  $\text{NO}_2$ ) in the naphthalene ring depends on the strength of sulphuric acid used in nitration. With 90% sulphuric acid 4 groups can enter, and with 100% sulphuric acid only 3.

(i)  $\alpha$ -Nitronaphthalene-3:6-disulphonic Acid (Alén's [ $\alpha$ ]acid; Freund's acid) is obtained by nitrating sodium naphthalene-2:7-disulphonate (33 parts) dissolved in sulphuric acid (50 parts), with 50% nitric acid (25 parts) in the cold. Or, if the product is to be used for reduction—as the presence of  $\alpha$ -nitronaphthalene-3:7-disulphonic acid is then of no consequence—the melt, which also contains naphthalene-2:6-disulphonic acid, obtained by sulphonating naphthalene (1 part) with sulphuric acid (5 parts) at 160° for 8 hours, is nitrated with 50% nitric acid (2 parts) in the cold (Freund, G.P. 27346; B.P. 1069, 1883; cf. Armstrong and Wynne, Proc. C.S. 1895, 11, 82). Its chloride is formed, together with the 1:8-dinitronaphthalene-3:6-disulphonyl chloride by nitrating naphthalene-2:7-disulphonyl chloride with nitrosulphuric acid at the ordinary temperature (Alén, Bull. Soc. chim. 1883, [ii], 39, 63).

**Identification.**—The acid and salts crystallise in small needles; the barium salt,  $\text{BaA} + 5\text{H}_2\text{O}$ ,

is sparingly, the potassium salt,  $\text{K}_2\text{A} + 3\text{H}_2\text{O}$ , and sodium salt,  $\text{Na}_2\text{A} + 6\text{H}_2\text{O}$ , are readily soluble in water. The chloride forms needles, m.p. 140-141°, convertible into 1:3:6-trichloronaphthalene (Alén, Förhandl. 1884, 2, 95; Cleve, Ber. 1892, 25, 2487; Armstrong and Wynne, l.c.).

**Reactions.**—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-3:6-disulphonic acid, and electrolytically into 1-amino-4-naphthol-3:6-disulphonic acid. With sodium amalgam it gives  $\alpha$ -naphthylamine (Alén, Förhandl. 1883, 8, 3).

(ii)  $\alpha$ -Nitronaphthalene-3:7-disulphonic Acid (Alén's [ $\beta$ ]acid) is obtained by nitration of naphthalene-2:6-disulphonic acid, as described for the 3:6-disulphonic acid (Freund, l.c.). Its chloride is formed, as sole product, when naphthalene-2:6-disulphonyl chloride is nitrated with nitrosulphuric acid (Alén, Bull. Soc. chim. 1883, [ii], 39, 64).

**Identification.**—The barium salt,  $\text{BaA} + 2\text{H}_2\text{O}$ , tablets; calcium salt,  $\text{CaA} + 2\text{H}_2\text{O}$ , needles; potassium salt,  $\text{K}_2\text{A}$ , needles; and sodium salt,  $\text{Na}_2\text{A} + 2\text{H}_2\text{O}$ , needles, are less soluble than the salts of the 3:6-acid. The chloride (with 1 mol.  $\text{C}_6\text{H}_6$  from benzene) forms prisms, m.p. 190-192°, convertible into 1:3:7-trichloronaphthalene (Alén, Förhandl. 1884, 2, 95; Armstrong and Wynne, Proc. C.S. 1890, 6, 13).

**Reactions.**—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-3:7-disulphonic acid, and electrolytically into 4-amino- $\alpha$ -naphthol-2:6-disulphonic acid. With sodium amalgam it gives  $\alpha$ -naphthylamine (Alén, Förhandl. 1883, 8, 21).

(iii)  $\alpha$ -Nitronaphthalene-3:8-disulphonic Acid is formed as chief product, together with some  $\beta$ -nitronaphthalene-4:7-disulphonic acid by nitrating naphthalene-1:6-disulphonic acid or its salts (Schultz, Ber. 1890, 23, 77; cf. Armstrong and Wynne, Proc. C.S. 1891, 7, 27).

**Preparation.**—Sodium naphthalene- $\beta$ -sulphonate (50 parts), sulphonated with 2½-3 times its weight of 20% anhydro-acid at 100°, is cooled to 10-15°, and nitrated below 25° with nitric acid,  $\rho$  1.4 (22.5 parts), during about 2 hours (Ewer and Pick, G.P. 52724). Or, the product obtained by sulphonating either naphthalene (10 parts) with monohydrate (40 parts) (first at 80-95° and then for 10 hours at 110°) or naphthalene- $\beta$ -sulphonic acid melt (20 parts) with monohydrate (20 parts) at 110°, is nitrated below 25-30° with 8.4 parts of nitric acid,  $\rho$  1.38 (Badische, G.P.a. 9514; Bernthsen, Ber. 1889, 22, 3328). According to Friedländer, the product obtained by any of these methods contains at least four nitro-acids, of which the  $\alpha$ -nitronaphthalene-3:8-disulphonic acid constitutes only about 40% (Heumann, Anilinfarben, 1898, ii, 518). Owing to their sparing solubility in alkalis or brine, the alkali salts of the nitro-acids are easily separated from the nitration product after dilution with water, but the separation is unnecessary if the nitro-acid is to be used for reduction to  $\alpha$ -naphthylamine-3:8-disulphonic acid.

It is also obtained, together with  $\alpha$ -nitronaphthalene-4:8-disulphonic acid and small quantities of the corresponding  $\beta$ -nitrodisul-

phonic acids when the product formed by sulphonating naphthalene (10 parts) with 23% anhydro-acid (50 parts) in the cold is cooled with ice and nitrated with nitric acid,  $\rho$  1.45 (7 parts). This product is useful only for reduction to the amino-acids from which  $\alpha$ -naphthylamine-3:8-disulphonic acid can easily be separated (Aktienges., G.P. 45776; B.P. 4625, 1888).

**Salts.**—The salts crystallise in easily soluble needles; the potassium salt,  $K_2A$ , is almost insoluble in dilute caustic potash solution (Friedländer, Ber. 1895, 28, 1535).

**Reactions.**—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-3:8-disulphonic acid, but in neutral solution with sodium bisulphite it yields  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid. Digestion with concentrated caustic soda solution furnishes the basic sodium salt of 4-nitroso- $\alpha$ -naphthol-2:5-disulphonic acid.

(iv)  $\alpha$ -Nitronaphthalene-4:8-disulphonic Acid is obtained, together with the 3:8-disulphonic acid, when, as already described, a melt containing the naphthalene-1:5- and 1:6-disulphonic acids is nitrated (Aktienges., l.c.). It is also formed by nitrating naphthalene-1:5-disulphonic acid and separated from the accompanying  $\beta$ -nitronaphthalene-4:8-disulphonic acid (*q.v.*) by means of brine, in which the sodium salt of the latter is the less soluble (Cassella, G.P. 65997). Reduction converts it into  $\alpha$ -naphthylamine-4:8-disulphonic acid.

(v)  $\alpha$ -Nitronaphthalene-5:8-disulphonic Acid is formed when barium naphthalene-1:4-disulphonate (5 parts) mixed with sulphuric acid (30 parts) is nitrated at 10–15° with 25% nitric acid (3 parts). The product is free from isomers (Bayer, G.P. 70857; Gattermann, Ber. 1899, 32, 1156). Reduction in acid solution converts it into  $\alpha$ -naphthylamine-5:8-disulphonic acid.

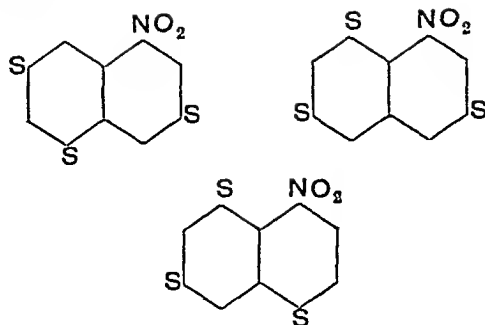
(vi)  $\beta$ -Nitronaphthalene-4:7-disulphonic Acid is formed together with  $\alpha$ -nitronaphthalene-3:8-disulphonic acid, by nitration of naphthalene-1:6-disulphonic acid (Schultz, *ibid.* 1890, 23, 77; Armstrong and Wynne, Proc. C.S. 1891, 7, 27). Reduction converts it into  $\beta$ -naphthylamine-4:7-disulphonic acid.

(vii)  $\beta$ -Nitronaphthalene-4:8-disulphonic Acid is obtained when naphthalene-1:5-disulphonic acid (28 parts) suspended in well-cooled sulphuric acid (90 parts) is nitrated with a mixture of nitric acid,  $\rho$  1.42 (10 parts), and sulphuric acid (10 parts). The product is poured on to ice, and soda (40 parts) added to separate the  $\beta$ -salt from the more soluble  $\alpha$ -salt (Cassella, G.P. 65997). It may be isolated as ferrous salt (Gen. Aniline Works Inc., U.S.P. 1968964) or as nickel, cobalt, manganese, or zinc salts (Tinker, U.S.P. 1836204). According to Montecatini (B.P. 514129) increased yield is obtained by nitrating naphthalene-1:5-disulphonic in concentrated sulphuric acid (oleum) medium.

Reduction converts it into  $\beta$ -naphthylamine-4:8-disulphonic acid.

#### Nitronaphthalenetrisulphonic Acids.

Three nitronaphthalenetrisulphonic acids are obtained from the corresponding naphthalenetrisulphonic acids by nitration



and two of them, the 3:6:8- and the 4:6:8-isomers, are important in connection with the manufacture of the H- and K- (aminonaphthol-disulphonic) acids.

(i)  $\alpha$ -Nitronaphthalene-3:5:7-trisulphonic Acid, formed when sodium naphthalene-1:3:7-trisulphonate, dissolved in sulphuric acid, is nitrated at 15–20°, can be separated by the addition of salt to the product after dilution with water (Cassella, G.P. 75432). Reduction converts it into  $\alpha$ -naphthylamine-3:5:7-trisulphonic acid.

(ii)  $\alpha$ -Nitronaphthalene-3:6:8-trisulphonic Acid is obtained by the nitration of naphthalene-1:3:6-trisulphonic acid. For technical purposes, the mixture obtained by sulphonating naphthalene-1:6- or -2:7-disulphonic acid is cooled to 25–30°, and nitrated at this temperature with the calculated quantity of nitric acid (Koch, G.P. 56058; B.P. 9258, 1890).

**Salts.**—The lead,  $Pb_3A_2 + 8H_2O$ ; barium,  $Ba_3A_2 + 8H_2O$ ; sodium,  $Na_3A + 6H_2O$ ; and aniline,  $B_3A + 2\frac{1}{2}H_2O$ , salts crystallise in needles (Fierz and Schmidt, Helv. Chim. Acta, 1921, 4, 381).

**Reactions.**—Reduction in acid solution converts it into  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid. Digestion with ammonia at 150–170° furnishes  $\beta$ -naphthylamine-3:6:8-trisulphonic acid (Kalle, G.P. 176621).

(iii)  $\alpha$ -Nitronaphthalene-4:6:8-trisulphonic Acid is produced by the nitration of sodium naphthalene-1:3:5-trisulphonate, the trisulphonic acid melt formed by sulphonating naphthalene-1:5-disulphonic acid (1 mol.) with anhydro-acid being diluted to a density of 66° Bé. at 15°, cooled to 5°, and the calculated quantity of nitric acid (1 mol.), mixed with sulphuric acid, added at this temperature (Bayer, G.P.a. 7004; B.P. 17141c, 1893; cf. Kalle, G.P.a. 11104; G.P. 82563; B.P. 1641, 1894). Reduction converts it into  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid.

#### DINITRONAPHTHALENES.

Two dinitronaphthalenes, the 1:5- and 1:8-compounds, are obtained when naphthalene or  $\alpha$ -nitronaphthalene is nitrated with concentrated nitric acid or with a mixture of nitric and sulphuric acids (or by nitrogen tetroxide, Schorigin, J. Gen. Chem. Russ. 1938, 8, 981). The proportion in which they are formed varies to some extent, but may be taken as 1:2 (Friedländer and Scherzer, Chem. Zentr. 1900, I, 410), although according to Gassmann, who used more concentrated acid mixtures, the best yield of 1:8-dinitronaphthalene (about 70%) is obtained

only when the temperature beyond the stage of mononitration is the lowest possible (Ber. 1896, 29, 1244, 1521). The range of dinitronaphthalenes has been extended by dehydrogenating the corresponding tetralin derivatives.

(i) 1:2-Dinitronaphthalene, m.p. 152°, is prepared from *ar*-1:2-dinitrotetralin by dibromination followed by dehydrobromination by heat (Vesely and Dvorak, Bull. Soc. chim. 1923, [iv], 33, 321).

(ii) 1:3-Dinitronaphthalene ([ $\gamma$ ]-dinitronaphthalene) is prepared from diazotised 2:4-dinitro-1-naphthylamine, but special care is necessary to avoid formation of the diazo-oxide. (Hodgson and Walker, J.C.S. 1933, 1620). The diazotisation is best carried out in a mixture of concentrated sulphuric acid and glacial acetic acid below 10°; the diazo compound is reduced by addition of cuprous oxide, and the dinitronaphthalene isolated by diluting the mixture, filtering the precipitate and purifying it by extraction with and crystallisation from pyridine. It forms pale yellow crystals, m.p. 146–147° (Hodgson and Birtwell, *ibid.* 1943, 433). It has also been obtained by oxidising *ar*-1:3-dinitrotetralin (Vesely and Dvorak, Bull. Soc. chim. 1923, [iv], 33, 323, 328). According to Fierz-David and Sponagel, no trace of 1:3-dinitronaphthalene is formed in the nitration of naphthalene (*l.c.*).

(iii) 1:4-Dinitronaphthalene, m.p. 131–132°, is prepared from 1-nitro-4-amino-5:6:7:8-tetrahydronaphthalene by diazotisation and treatment with sodium nitrite followed by dehydrogenation (Chudozilov, Chem. Listy, 1926, 20, 509).

(iv) 1:5-Dinitronaphthalene ([ $\alpha$ ]-dinitronaphthalene) is obtained as minor product, together with the 1:8-compound, when  $\alpha$ -nitronaphthalene (10 parts) dissolved in sulphuric acid (60 parts) is nitrated at 0° by a mixture of nitric acid,  $\rho$  1.4 (5.2 parts), with sulphuric acid (26 parts). The solution, at first red, becomes white owing to the separation of the mixed dinitronaphthalenes as a thick magma, which when dry melts at about 140°. The mixture of dinitronaphthalenes finds some application in blasting explosives. To isolate its constituents, this solid product is not removed from the spent acid, but at the close of the nitration is heated with it at 80–90° until completely dissolved and the solution then cooled to 20°, whereby an almost complete separation of the 1:5-isomer is achieved. From the filtrate, the remainder of the nitration product is precipitated by the addition of water, and the 1:8-derivative extracted from the dried precipitate by pyridine in which 1:5-dinitronaphthalene is only sparingly soluble (Friedländer, Ber. 1899, 32, 3531; Kalle, G.P. 117368. Finzi, Annali Chim. Appl. 1925, 15, 55). 1:5-Dinitronaphthalene can be separated from the nitration mixture by the aid of concentrated sulphuric acid or of aniline (Voroshnev and Kulev, Ber. 1929, 62 [B], 934) or by boiling sodium sulphite solution which dissolves only the 1:8-isomer (Hodgson and Walker, J.C.S. 1933, 1346); and the 1:8-isomeride by conversion of the 1:5-compound into either naphthazarin (Gallotti and Galimberti, A. 1932, 1123) or 5-nitro- $\alpha$ -naphthylamine (Hodgson and Walker,

*l.c.*). The removal of the 1:8-derivative can also be effected by extraction of the dry nitration product with acetone (Beilstein and Kurbatow, Annalen, 1880, 202, 219), chloroform (Darmstadter and Wichelhaus, *ibid.* 1869, 152, 301), benzene (Aguar, Ber. 1870, 3, 29; Beilstein and Kuhlberg, Annalen, 1873, 169, 85), or acetic acid (Aguar, Ber. 1872, 5, 372).

Alternatively, the mixture of dinitronaphthalenes (200 parts), obtained technically in the form of a 60% paste, is heated at 80–90° during 5–6 hours with 40% sodium bisulphite solution (740 parts) and 25% ammonia (140 parts) and the insoluble 1:5-dinitronaphthalene then removed by filtration. In this case the filtrate contains not 1:8-dinitronaphthalene, but  $\alpha$ -naphthylsulphamino-4:7-di- and -2:4:7-tri-sulphonic acids arising from the interaction of this dinitro-compound with the bisulphite (Höchst, G.P. 221383).

*Properties.*—1:5-Dinitronaphthalene crystallises from acetic acid in six-sided yellow needles, m.p. 216° (Aguar, Ber. 1872, 5, 372). It is only sparingly soluble in the ordinary solvents, and practically insoluble in carbon disulphide or cold nitric acid. With phosphorus pentachloride it yields 1:5-dichloronaphthalene (Atterberg, *ibid.* 1876, 9, 1188, 1730). It is used technically in the production of naphthazarin (*q.v.*, p. 384a). It forms mixed crystals, m.p. 145°, with 1:8-dinitronaphthalene containing 78% of the latter (Fierz-David and Sponagel, *l.c.*).

*Reactions.*—Reduction with alcoholic ammonium sulphide converts it into 5-nitro- $\alpha$ -naphthylamine and 1:5-diaminonaphthalene, but in acid solution only the latter is obtained. Digestion with ammonium sulphite or sodium bisulphite solution furnishes 1:5-diaminonaphthalenedisulphonic acid.

When heated with 12–23% anhydro-acid at 40–50° it yields 8-nitroso- $\alpha$ -naphthol, but if a reducing agent, such as sulphur or zinc, be present, a naphthazarin intermediate product is formed from which naphthazarin (5:8-dihydroxy- $[\alpha]$ -naphthaquinone) can be isolated.

(v) 1:6-Dinitronaphthalene ([ $\delta$ ]-dinitronaphthalene) is obtained by boiling diazotised 1:6-dinitro- $\beta$ -naphthylamine with alcohol. It crystallises from alcohol in bright yellow needles, m.p. 161.5° (Graebe and Drews, Ber. 1884, 17, 1170; cf. Kehrman and Matis, Ber. 1898, 31, 2419). It has also been obtained, m.p. 160–162°, from 1:6-nitroaminonaphthalene by diazotisation and treatment with sodium nitrite (Vesely and Dvůřák, *l.c.*).

(vi) 1:7-Dinitronaphthalene, m.p. 156°, from 1:7-nitroaminonaphthalene by diazotisation and treatment with sodium nitrite (Vesely and Dvůřák, *l.c.*).

(vii) 1:8-Dinitronaphthalene ([ $\beta$ ]-dinitronaphthalene) is the major product of the dinitration of naphthalene. For its separation, see 1:5 dinitronaphthalene.

*Properties.*—1:8-Dinitronaphthalene crystallises in large, yellow rhombic plates, m.p. 172° (Friedländer, *l.c.*). In ordinary solvents, and in concentrated sulphuric acid, it is more soluble than the 1:5 compound. According to Beilstein and Kuhlberg (Annalen, 1873, 169, 86), 1 part

dissolves in 91.4 parts of chloroform, in 530 parts of 88% alcohol, or in 139 parts of benzene at 19°; and according to Friedländer, 1 part dissolves in 10 parts of cold or in 1.5 parts of hot pyridine. With phosphorus pentachloride it yields 1:8-dichloronaphthalene in small quantity, the chief product being 1:4:8-trichloronaphthalene (Atterberg, l.c.).

**Reactions.**—Reduction in acid solution converts it into 1:8-diaminonaphthalene. Blue, violet, or black dyestuffs are obtained when 1:8-dinitronaphthalene is heated with alkali, sodium bisulphite solution, and reducing agents such as glucose (Badische, G.P. 79208; B.P. 10996, 1893; G.P. 88236; B.P. 7766, 1896), milk sugar, sodium stannite, or sodium sulphide (Badische, G.P. 92471; B.P. 20250, 1896); or, omitting alkali, with sodium sulphide (Badische, G.P. 84989; B.P. 10996, 1893; G.P. 88847; B.P. 22603, 1894), or sodium disulphide (Höchst, G.P. 117188; 117189). Digestion with sodium or ammonium sulphite solution at 70–90°, the alkali set free being removed as formed, yields  $\alpha$ -sulphaminonaphthyl-4:7-di- and -2:4:7-tri-sulphonic acids (whence by hydrolysis the corresponding  $\alpha$ -naphthylaminesulphonic acids are obtained), but boiling with sodium bisulphite solution furnishes 1:8-diaminonaphthalenetrisulphonic acid.

When heated with 12–23% anhydro-acid at 40–50°, it yields 5-nitro-4-nitroso- $\alpha$ -naphthol, but if it be heated with sulphuric acid and reducing agents, such as aniline or tin or iron, or its solution in sulphuric acid be electrolysed, a naphthazarin intermediate product is formed isomeric with that obtained from 1:5-dinitronaphthalene (Badische, G.P. 76922; 79406).

(viii) 2:3-Dinitronaphthalene, m.p. 170–5–171°, is prepared from 6-nitro-7-amino-1:2:3:4-tetrahydronaphthalene by the diazo-reaction to 6:7-dinitrotetrahydronaphthalene which is then dehydrogenated (Chudezilov, Chem. Listy, 1926, 20, 509). Hodgson and Turner prepared it from 2:3-dinitro-1-naphthylamine and found m.p. 159° (J.C.S. 1943, 635).

(ix) 2:6-Dinitronaphthalene, m.p. 279°, has been prepared from 6-nitro- $\beta$ -naphthylamine through the diazonium compound (Vesely and Jakes, Bull. Soc. chim. 1923, [iv], 33, 942) but the product had lower melting-point than that later made from 2:6-diaminonaphthalene by interaction of the tetrazo-compound with nitrite in presence of cupro-cupric sulphite (Chatt and Wynne, J.C.S. 1943, 33).

(x) 2:7-Dinitronaphthalene, m.p. 234°, is obtained when the dinitration product of naphthalic acid is decarboxylated with copper bronze and boiling quinoline (Rule and Brown, *ibid.* 1934, 171).

#### Dinitronaphthalenemonosulphonic Acids.

(i) 1:5-Dinitronaphthalene-3-(or 7-)sulphonic Acid is obtained when  $\alpha$ -nitronaphthalene-7-sulphonic acid, dissolved in sulphuric acid, is nitrated at 0–15°, and common salt added to the product after dilution with water (Cassella, G.P. 85058). It is also stated to be formed when 1:5-dinitronaphthalene, dissolved in 6 times its weight of monohydrate, is heated at 100–110° with rather more than twice its

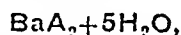
weight of 20% oleum (Höchst, G.P. 117268), but according to Eckstein this dinitronaphthalene is not sulphonated by 15–20% oleum at 140°, and at higher temperatures or with more concentrated acid is destroyed (Ber. 1902, 35, 3403).

**Identification.**—The sodium salt forms needles, soluble in 12 parts of boiling water; the chloride, prisms, m.p. 118° (Höchst, l.c.).

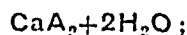
**Reactions.**—Reduction converts it into 1:5-diaminonaphthalene-3-sulphonic acid, but digestion with sodium sulphite or bisulphite solution gives a nitro- $\alpha$ -naphthylaminesulphonic acid. With oleum in presence of a reducing agent, a soluble blue intermediate product is obtained which yields a naphthazarinsulphonic acid when boiled with water.

(ii) 1:8-Dinitronaphthalene-3-(or 6-)sulphonic Acid is formed, together with the 1:5-dinitro-acid, when sodium naphthalene- $\beta$ -sulphonate, dissolved in sulphuric acid, is dinitrated below 10°, and is precipitated by stirring the product into twice its volume of brine, the 1:5-isomer remaining in solution (Cassella, G.P. 67017; B.P. 6972, 1891; G.P. 85058). It is also produced when 1:8-dinitronaphthalene, dissolved in monohydrate, is sulphonated at 100–110° with twice its weight of 20% oleum (Höchst, G.P. 117268; Eckstein, Ber. 1902, 35, 3403).

**Identification.**—The barium salt,



soluble in 8.5 parts of boiling or 20 parts of cold water (Eckstein, l.c.); calcium salt,



potassium salt, and sodium salt,  $\text{NaA} + \text{H}_2\text{O}$ , soluble in 6.5 parts of boiling water, crystallise in needles. The chloride forms monoclinic prisms, m.p. 143–144° (Höchst, l.c.; cf. Hellström, Förhandl. 1888, 10, 613).

(iii) 1:8-Dinitronaphthalene-4-(or 5-)sulphonic Acid is formed when the monosulphonation product of  $\alpha$ -nitronaphthalene, consisting chiefly of the 5-sulphonic acid, is nitrated at 15–20°, and the 1:8-dinitro-acid separated by stirring the mixture into brine (Cassella, G.P. 70019; B.P. 4613, 1893).

(iv) 2:4-Dinitronaphthalene-8-sulphonic Acid is obtained when naphthasultam or 2:4-dinitronaphthasultam is heated with fuming nitric acid (Dannert, J. Amer. Chem. Soc. 1907, 29, 1327).

#### Dinitronaphthalenedisulphonic Acids.

(i) 1:5-Dinitronaphthalene-3:7-disulphonic Acid is obtained when sodium naphthalene-2:6-disulphonate (or  $\alpha$ -nitronaphthalene-3:7-disulphonate), dissolved in sulphuric acid, is dinitrated (or nitrated) at 20–30°, and the product salted out (Cassella, G.P. 61174; B.P. 15346, 1890; cf. Oehler, G.P.a. 1430; Bayer, G.P. 126198).

**Reactions.**—Reduction in acid solution converts it into 1:5-diaminonaphthalene-3:7-disulphonic acid. When dissolved in monohydrate and heated at 50° with a solution of sulphur in 20% anhydro-acid, it gives a blue mordant dyo of the naphthazarin "intermediate product" type (Bayer, l.c.).



(ii) 1:6-Dinitronaphthalene-3:8-disulphonic Acid, obtained by nitration of  $\alpha$ -nitronaphthalene-3:8-disulphonic acid or of naphthalene-1:6-disulphonic acid has not been characterised. Reduction in acid solution converts it into 1:6-diaminonaphthalene-3:8-disulphonic acid (Friedländer and Kielbasinski, Ber. 1896, 29, 1982).

(iii) 1:6-Dinitronaphthalene-4:8-disulphonic Acid is obtained when sodium naphthalene-1:5-disulphonate (or its mononitration product), dissolved in monohydrate, is dinitrated (or nitrated) below 30°. The product is free from isomers (Kalle, G.P. 72665), and on reduction in acid solution yields 1:6-diaminonaphthalene-4:8-disulphonic acid (Friedländer and Kielbasinski, l.c.).

(iv) 1:8-Dinitronaphthalene-3:6-disulphonic Acid is obtained free from isomers when sodium naphthalene-2:7-disulphonate, dissolved in sulphuric acid, is dinitrated at 20–30° (Cassella, G.P. 67062; B.P. 1742, 1891; Bayer, G.P. 69190; B.P. 11522, 1892). Its chloride is formed, together with the mononitro-derivative, by nitrating naphthalene-2:7-disulphonyl chloride (Alén, Forhändl. 1883, 8, 13).

**Identification.**—The barium salt,  $BaA + 5H_2O$ , prisms, and the potassium salt needles,  $K_2A$ , from hot, or  $K_2A + 4H_2O$  from cold solution, are easily soluble. The chloride has m.p. 219°; with 1 mol.  $C_6H_6$  it forms needles (Alén, l.c.).

**Reactions.**—Reduction in acid solution converts it into 1:8-diaminonaphthalene-3:6-disulphonic acid, but digestion with sodium sulphite or bisulphite solution gives 1-amino-8-naphthol-3:6-disulphonic acid. With dilute caustic soda solution in the cold, it forms sodium 5-nitro-4-nitroso- $\alpha$ -naphthol-2:7-disulphonate, but 4:5-dinitrosodihydroxynaphthalene-2:7-disulphonate if the solution be concentrated.

#### TRINITRONAPHTHALENES.

Three trinitronaphthalenes, the 1:2:5-, 1:3:5-, and 1:4:5-derivatives, are obtained by the nitration of 1:5-dinitronaphthalene, and a fourth, the 1:3:8-derivative, by the nitration of 1:8-dinitronaphthalene. The constitution of these compounds has been determined by oxidation to the respective nitrophthalic acids.

Melting-point curves of the various binary and ternary mixtures of  $\alpha$ -nitronaphthalene, 1:5- and 1:8-dinitronaphthalenes, and 1:2:5-, 1:3:5-, 1:3:8-, and 1:4:5-trinitronaphthalenes have been determined by Pascal and the results applied to the analysis of the products of the nitration of naphthalene (Bull. Soc. chim. 1920, [iv], 27, 388).

(i) 1:2:5- or  $[\delta-]$ Trinitronaphthalene (Will, Ber. 1895, 28, 377) crystallises from alcohol in needles, m.p. 112–113°. Dimroth and Ruck suggest that this is a mixture of 1:3:5- and 1:4:5-isomers (Annalen, 1925, 446, 123).

(ii) 1:3:5- or  $[\alpha-]$ Trinitronaphthalene crystallises from alcohol in scales, m.p. 122° (Aguiar, Ber. 1872, 5, 373, 897), 119–5° (Dimroth and Ruck, l.c.). It forms a molecular compound, m.p. 146–148° with  $\beta$ -naphthol.

(iii) 1:4:5- or  $[\gamma-]$ Trinitronaphthalene (Beilstein and Kuhlberg, Annalen, 1873, 169, 97; cf. Will, l.c.) crystallises from chloroform

in bright yellow scales, m.p. 154° (Aguiar, l.c. 903), 148–149° (Dimroth and Ruck, l.c.). It is stated to be explosive (Haid *et al.*, Chem. Zentr. 1931, I, 2426).

(iv) 1:3:8- or  $[\beta-]$ Trinitronaphthalene (Beilstein and Kuhlberg, l.c.; Friedländer, Ber. 1899, 32, 3531). From the mixed dinitronaphthalenes obtained by the nitration of  $\alpha$ -nitronaphthalene (10 parts), the greater part of the 1:5-derivative can be separated by Kalle's method as already described (*see* 1:5-dinitronaphthalene). The mother-liquor contains mainly the 1:8-derivative, and, by the addition of a mixture of nitric acid of  $\rho$  1.4 (3.3 parts) with sulphuric acid (10 parts) gives a crystalline separation of 1:3:8-trinitronaphthalene in needles, m.p. 218° (Kalle, G.P. 117638). It dissolves in cold sodium bisulphite solution without undergoing change, but is converted into nitroaminonaphtholsulphonic acids when the solution is warmed (Friedländer and Scherzer, Chem. Zentr. 1900, I, 410).

#### TETRANITRONAPHTHALENES.

Five tetranitronaphthalenes are described, obtained by further nitration of 1:5, 1:8-, or 2:6-dinitronaphthalenes or from trinitronaphthalenes.

(i)  $[\alpha-]$ Tetranitronaphthalene, which melts at 259° (Beilstein and Kuhlberg, Annalen, 1873, 169, 99; Aguiar, Ber. 1872, 5, 374).

(ii) 1:3:5:7-Tetranitronaphthalene, m.p. 260°, has been prepared by nitration of 2:6-dinitronaphthalene (Chatt and Wynne, J.C.S. 1943, 33).

(iii) 1:3:5:8- $[\gamma-]$ Tetranitronaphthalene, prepared by nitration of 1:4:5-trinitronaphthalene (Dimroth and Ruck, l.c.), m.p. 194–195° (Will, Ber. 1895, 28, 377).

(iv) 1:4:5:8- $[\delta-]$ Tetranitronaphthalene. This compound is now known to be the one formerly called by Will (l.c.) the 1:2:5:8-isomer. It is prepared by nitration of 1:4:5-trinitronaphthalene (along with the 1:3:5:8-isomer) and has m.p. 340–345°. *See also* Dimroth and Roos, Annalen, 1927, 456, 178.

(v) 1:3:6:8- $[\beta-]$ Tetranitronaphthalene melts at 230° (Aguiar, l.c.; Will, l.c.).

#### CHLORONITRONAPHTHALENES.

The nitro-derivatives of the chloronaphthalenes can be prepared in the following ways to which reference will be given under individual compounds.

1. Chlorination of nitronaphthalene.
2. Nitration of chloronaphthalenes.
3. Replacement of amino-group of nitronaphthylamines by chlorine by Sandmeyer reaction.
4. Replacement of sulphonic group by chlorine by aqueous chlorination of nitronaphthalenesulphonic acids.
5. Heating of nitronaphthalene di- and tetrachlorides to give mono- and di-chloronitronaphthalenes.

Nitration of  $\alpha$ -chloronaphthalene with a mixture of nitric and sulphuric acids gives a mixture of 1:4-, 1:6-, and 1:8-chloronitronaphthalenes. With increase of temperature the proportion of



1:5-isomer decreases from 18.5% to nil with a corresponding increase in the proportion of 1:4-isomer from 47% to 63.5%; the 1:8-isomer remaining constant at 36.5%. Employing modified nitration conditions the formation of 1:8-isomer can be increased to 65.2% (Ferrero and Caffisch, *Helv. Chim. Acta*, 1928, 11, 795). A study of mixtures of isomeric chloronitronaphthalenes showed the following eutectics (Asaoka, B. 1929, 972):

1:4 (57%)	1:5 (43%)	m.p. 74-75°
1:4 (57%)	1:8 (43%)	m.p. 52-53°
1:5 (45%)	1:8 (55%)	m.p. 66-67°

Dinitration of  $\alpha$ -chloronaphthalene gives a mixture of 4-chloro-1:5-dinitronaphthalene and 4-chloro-1:8-dinitronaphthalene, whilst trinitration gives a mixture of 4-chloro-1:3:8-trinitronaphthalene and 4-chloro-1:3:5-trinitronaphthalene.

Chlorination of  $\alpha$ -nitronaphthalene with ferric chloride catalyst gives a mixture of the 5- and 8-chloro-derivatives and by dichlorination mainly 5:8-dichloro- $\alpha$ -nitronaphthalene.

#### *Monochloronitronaphthalenes.*

(i) 2-Chloro- $\alpha$ -nitronaphthalene, m.p. 95.5°, is produced by electrolysis of a solution of diazotised 1-nitro- $\beta$ -naphthylamine in presence of cuprous chloride (Vesely, Ber. 1905, 38, 137).

(ii) 3-Chloro- $\alpha$ -nitronaphthalene, m.p. 105°, has been prepared by chlorination of 4-nitroacet- $\alpha$ -naphthylamide, hydrolysis of the acetyl group to give 2-chloro-4-nitro- $\alpha$ -naphthylamine and removal of the amino-group by diazotisation and reaction with alcohol (Hodgson and Elliott, J.C.S. 1934, 1705).

(iii) 4-Chloro- $\alpha$ -nitronaphthalene, m.p. 85°, is produced as chief product along with the 5- and 8-isomers when  $\alpha$ -chloronaphthalene is nitrated in the cold (Atterberg, Ber. 1876, 9, 927; Ferrero and Caffisch, *Helv. Chim. Acta*, 1928, 11, 795; Griesheim, G.P. 120585). It has been prepared from 4-nitro- $\alpha$ -naphthylamine by Sandmeyer reaction (Franzen and Helwert, Ber. 1920, 53 [B], 320).

*Reactions.*—Reaction with alcoholic ammonia at 170° gives 4-nitro- $\alpha$ -naphthylamine (Griesheim, G.P. 117006) and with alkali-hydroxides, carbonates or acetates at 150° gives 4-nitro- $\alpha$ -naphthol (Griesheim, G.P. 117731).

(iv) 5-Chloro- $\alpha$ -nitronaphthalene, m.p. 111°, is prepared by chlorination of  $\alpha$ -nitronaphthalene in the presence of ferric chloride, 8-chloro- $\alpha$ -nitronaphthalene being simultaneously formed (Aktienges., G.P. 99758). It is also formed in small degree by nitration of  $\alpha$ -chloronaphthalene (Griesheim, G.P. 120585) and by aqueous chlorination under acidic conditions of 5-nitronaphthalene- $\alpha$ -sulphonic acid when the sulphonic group is replaced by chlorine (Armstrong and Williamson, Proc. C.S. 1886, 2, 233; cf. Kalle, G.P. 343147).

(v) 7-Chloro- $\alpha$ -nitronaphthalene, m.p. 116°, is formed by nitration of  $\beta$ -chloronaphthalene (Armstrong and Wynne, *ibid.* 1889, 5, 71).

(vi) 8-Chloro- $\alpha$ -nitronaphthalene, m.p. 94°, is obtained as chief product along with 5-chloro-1-nitronaphthalene when  $\alpha$ -nitronaphtha-

lene is chlorinated, using ferric chloride as catalyst, and crystallises from the reaction mass (Aktienges., G.P. 99758; Ullmann and Consonno, Ber. 1902, 35, 2808). Another method proposed for manufacture is by nitration of naphthalene dichloride and heating the nitro-naphthalene dichloride, when hydrogen chloride is split off giving 8-chloro- $\alpha$ -nitronaphthalene (Matter, G.P. 317755). It is also produced by aqueous chlorination of 8-nitronaphthalene- $\alpha$ -sulphonic acid (Kalle, G.P. 343107; Voroschov and Kozlov, Ber. 1936, 69 [B], 412). It is formed in small amount by nitration of  $\alpha$ -chloronaphthalene.

*Reactions.*—With sulphuric acid at 80°, 8-chloro- $\alpha$ -nitronaphthalene-5-sulphonic acid is formed whereas 5-chloro- $\alpha$ -nitronaphthalene remains unsulphonated (Aktienges., G.P. 103950). With water or aqueous alkali 8-chloro- $\alpha$ -nitronaphthalene is hydrolysed to 8-chloro- $\alpha$ -naphthol (Voroschov and Kozlov, *l.c.*).

#### *Dichloronitronaphthalenes.*

(i) 4:7-Dichloro- $\alpha$ -nitronaphthalene, m.p. 119°, is produced by nitration of 1:6-dichloronaphthalene with fuming nitric acid (Cleve, Bull. Soc. chim. 1878, [ii], 29, 499).

(ii) 4:8-Dichloro- $\alpha$ -nitronaphthalene, m.p. 142°, is formed by nitration of 1:5-dichloronaphthalene (Atterberg, Ber. 1876, 9, 928).

(iii) 5:8-Dichloro- $\alpha$ -nitronaphthalene, m.p. 94°, is produced by chlorination of  $\alpha$ -nitronaphthalene at 60-80° with ferric chloride catalyst (Baeyer, G.P. 293318). It can also be produced by aqueous chlorination of 5-chloro-8-nitronaphthalene- $\alpha$ -sulphonic acid when the sulphonic group is replaced by chlorine (Kalle, G.P. 343147). Naphthalene tetrachloride by nitration and elimination of 2 mol. of hydrogen chloride from the nitronaphthalene tetrachloride gives 5:8-dichloro- $\alpha$ -nitronaphthalene (Matter, G.P. 317755; 348009).

#### *Chlorodinitronaphthalenes.*

(i) 1-Chloro-2:4-dinitronaphthalene, m.p. 146.5°, is obtained by heating 2:4-dinitro- $\alpha$ -naphthol with toluene-*p*-sulphonyl chloride in dimethylaniline (Ullmann, G.P. 193318).

*Reactions.*—The chlorine group is very mobile, being of the same order of reactivity as the chlorine in 1-chloro-2:4-dinitrobenzene (Talen, Rec. trav. chim., 1928, 47, 329; Mangini and Frenguelli, Gazzetta, 1937, 67, 358, 373). With sodium azide there is formed 2:4-dinitro- $\alpha$ -naphthylazide which, with sulphuric acid, is converted to 4-nitro- $[\beta]$ -naphthaquinonediazoxide peroxide. Kehrman (Ber. 1923, 56 [B], 2385) describes a series of quinoneimide dyestuffs prepared from 1-chloro-2:4-dinitronaphthalene.

(ii) 1-Chloro-4:8-dinitronaphthalene, m.p. 138°, is produced by nitration of dichloronaphthalene (Atterberg, *ibid.* 1876, 9, 927) or by nitration of 8-chloro-1-nitronaphthalene (Ullmann and Consonno, *ibid.* 1902, 35, 2810).

*Reactions.*—With ammonia there is produced 4:8-dinitro- $\alpha$ -naphthylamine and with aqueous sodium carbonate 4:8-dinitro- $\alpha$ -naphthol (Ullmann and Consonno, *l.c.*).

(iii) 1-Chloro-4:5-dinitronaphthalene, m.p. 180°, is obtained by dinitration of  $\alpha$ -

chloronaphthalene (Atterberg, *ibid.* 1876, 9, 928) or by nitration of 5-chloro- $\alpha$ -naphthoic acid (Ekstrand, J. pr. Chem. 1888, [iii], 38, 171).

#### *Dichlorodinitronaphthalenes.*

A mixture of dichloro-1:5- and -1:8-dinitronaphthalenes is formed by dichlorination of the respective dinitronaphthalene in a fused state in the presence of ferric chloride (Pollak, G.P. 134306).

4-Chloro-1:3:8-trinitronaphthalene, m.p. 143–144°, is obtained along with 4-chloro-1:3:5-trinitronaphthalene by trinitration of  $\alpha$ -chloronaphthalene. By heating it with dilute caustic alkali 2:4:8-trinitro- $\alpha$ -naphthol is formed (Rindl, J.C.S. 1913, 103, 1911).

#### NAPHTHYLAMINES.

Both  $\alpha$ - and  $\beta$ -naphthylamine and their sulphonic acid derivatives are of considerable technical importance. Synthetic routes to the  $\beta$ -naphthylamine series are necessarily different from those to the  $\alpha$ -series, since nitration of naphthalene derivatives rarely occurs in the  $\beta$ -position.  $\alpha$ -Naphthylamine is obtained by reduction of  $\alpha$ -nitronaphthalene, and its sulphonic acids by sulphonation of the amine, or by nitration of naphthalenesulphonic acids followed by reduction;  $\beta$ -naphthylamine is obtained from  $\beta$ -naphthol, its sulphonic acids by sulphonation of the base or from  $\beta$ -naphthol-sulphonic acids, e.g., by the Bucherer reaction. Only two  $\beta$ -naphthylaminedisulphonic acids, namely the 4:7- and 4:8-acids, are obtained by nitration of naphthalenedisulphonic acids followed by reduction.

The two naphthylamines and certain of their sulphonic acids are used as first, middle, or end components of azo-dyes; the sulphonic acids are also used in the manufacture of naphtholsulphonic acids, aminonaphtholsulphonic acids, or dihydroxynaphthalenesulphonic acids, which find extensive employment in the production of azo-dyes. The differences in the mode of coupling with diazotised bases in the two series have already been discussed (*see* p. 272d).

#### $\alpha$ -Naphthylamine.

$\alpha$ -Naphthylamine (1-aminonaphthalene) can be obtained from  $\alpha$ -nitronaphthalene by the action of many reducing agents of which iron with aqueous hydrochloric acid or ferrous chloride is as good as any. Several publications describe catalytic hydrogenation (*see* Sabatier and Senderens, *Compt. rend.* 1902, 135, 225; Poma and Pelligrini, B.P. 227481; Parrett and Lowry, J. Amer. Chem. Soc. 1926, 48, 778; I.G., B.P. 260186; Seldon Co., B.P. 304640).

It can be obtained by the interaction of  $\alpha$ -chloronaphthalene with ammonia solution and a copper catalyst (Groggin and Stirton, *Ind. Eng. Chem.* 1936, 28, 1051). It is also obtained when  $\alpha$ -naphthol is heated with ammonia under pressure at 150–160° for 60–70 hours (Badische, G.P. 14612). The yield may reach 70% of that calculated if the naphthol be heated with ammonia-calcium chloride at 270° for 8 hours, but dinaphthylamine is also formed in quantities varying with the conditions employed (Benz,

Ber. 1883, 16, 14). Substitution of acetamide at 270° for ammonia gives a 50% yield of acet- $\alpha$ -naphthalide, together with about 15% of dinaphthylamine (Calm, *ibid.* 1882, 15, 615), but replacement of ammonia by sodamide at 220° leads to the production of 5-amino- $\alpha$ -naphthol (Sachs, G.P. 181333).

*Manufacture.*—The method of manufacture is essentially that which has been described by Witt (*Chem. Ind.* 1887, 10, 218; Paul, *Z. angew. Chem.* 1897, 10, 145), with improvements due to experience.  $\alpha$ -Nitronaphthalene is reduced with iron borings and a small amount of hydrochloric acid in a cast-iron reduction pan with stirrer, condenser, and arrangements for controlling the temperature. Enough water is used to keep the mass stirrable. When reduction is complete, different methods may be used for separating the naphthylamine, after neutralising acid, e.g., vacuum distillation, steam distillation, or solvent extraction. The crude  $\alpha$ -naphthylamine is purified by distillation. Precautions must be taken to protect the workers from contact with  $\alpha$ -naphthylamine. The product contains  $\beta$ -naphthylamine from which it may be freed either by repeated crystallisation from warm light petroleum, in which the  $\beta$ -base is the more soluble (Erdmann, *Annalen*, 1893, 275, 217, footnote), or warming it with 10% of its weight of xylene, allowing the homogeneous mixture to cool, breaking up the semi-solid mass and separating the pure crystalline  $\alpha$ -base in a centrifuge (Weiler-ter-Meer, G.P. 205076; B.P. 16446, 1907). The residue left after evaporation of the mother-liquor to dryness contains both bases: if it is dissolved in hot dilute hydrochloric acid, most of the  $\alpha$ -base separates as the crystalline hydrochloride on cooling, while from the filtrate the  $\beta$ -base is precipitated as sulphate by the addition of dilute sulphuric acid (Weiler-ter-Meer, *loc. cit.*; cf. F. Reverdin and E. Nölting, "Sur la constitution de la Naphthaline," *ed.* 1885, 35).

*Properties.*—Pure  $\alpha$ -naphthylamine has m.p. 49.2–49.3°; its f.p. is 48.61–48.63°. Technical  $\alpha$ -naphthylamine has f.p. of 45.3–45.5° and contains not more than 95.5%  $\alpha$ -naphthylamine,  $\beta$ -naphthylamine always being present (Gubelmann and Weiland, *Ind. Eng. Chem.* 1929, 21, 1239; cf. Lenkhold and Ostroumov, A. 1930, 1174; Lenkhold, *ibid.*). It boils at 300° (Zinin, J. pr. Chem. 1842, 27, 141) and is only slightly volatile in steam. It is easily soluble in alcohol, ether, or aniline but almost insoluble in water, of which 100 c.c. dissolve only about 0.167 g. at the ordinary temperature (Ballé, Ber. 1870, 3, 288, 673). On exposure to the air, the technical product changes colour gradually to greyish-violet, owing possibly to the presence of a small quantity of 1:8-diaminonaphthalene (Witt, *loc. cit.*). Its odour is characteristic and unpleasant.

The salts are for the most part sparingly soluble in water. The *hydrochloride*,  $B, HCl$ , and the *sulphate*,  $B_2, H_2SO_4 + 2H_2O$ , form scales; the *platinichloride*,  $(B, HCl)_2PtCl_4$ , is a crystalline powder. The *picrate*,  $B, HA$ , forms sparingly soluble prisms, m.p. 161° (Smolka, *Monatsh.* 1885, 6, 923; cf. Suida, Ber. 1908, 41, 1913).

**Reactions.**—Diazotised, it forms the first component of many azo-dyes. It also couples with diazotised bases forming the middle or end component of disazo-dyes. From its diazo-compound, *a*-naphthol can be obtained, and is also formed when *a*-naphthylamine hydrochloride or sulphate is digested with water at 200°. By sulphonation, it furnishes a series of *mono*-, *di*-, and *tri*-sulphonic acids. Reduction in boiling amyl alcoholic solution with sodium converts it into *ar*-tetrahydro-*a*-naphthylamine. When heated with zinc chloride or calcium chloride at 280° it undergoes partial decomposition into *aa'*-dinaphthylamine and ammonia (Benz, *ibid.* 1883, 16, 14).

Oxidised by potassium dichromate and dilute sulphuric acid it yields [*a*]-naphthaquinone and phthalic acid (Monnet, Reverdin, and Nölting, *ibid.* 1879, 12, 2306). but with oxidising agents such as ferric chloride, silver nitrate, mercuric chloride, or chromic acid, its salts in aqueous solution produce an azure-blue precipitate of "naphthamein," which rapidly becomes purple, dissolves in chloroform, and is not bleached by sulphurous acid (Piria, Annalen, 1851, 78, 64; Schiff, *ibid.* 1857, 101, 92; 1864, 129, 255).

With excess of nitrous gases and subsequent warming, *a*-naphthylamine hydrochloride suspended in water gives rise to 2-nitro-*a*-naphthol (Varma and Krishnamurthy, J. Indian Chem. Soc. 1926, 3, 326). It also forms blood-red compounds, m.p. 72° and 64.5°, with 1-chloro- and 1-bromo-2:4-dinitrobenzene (Buchler, Hisoy, and Wood, J. Amer. Chem. Soc. 1930, 52, 1939).

#### Acyl Derivatives.

**N-Formyl-*a*-naphthylamine**, obtained by boiling *a*-naphthylamine with 16.3% formic acid (6:2 parts) for  $\frac{1}{2}$  hour, crystallises from water in needles, m.p. 138.5° (Tobias, Ber. 1882, 15, 2447).

**N-Acetyl-*a*-naphthylamine** (*acet-a-naphthalide*) is formed by heating *a*-naphthol with ammonium acetate at 270–280° (Calm, *ibid.* 1882, 15, 615), and prepared by boiling *a*-naphthylamine with 1.25 times its weight of glacial acetic acid for 4–5 days (Liebermann and Dittler, Annalen, 1876, 183, 229). It crystallises in needles, m.p. 159°, is easily soluble in alcohol and acetic acid, and dissolves moderately in hot water but is almost insoluble in the cold (Liebermann and Dittler, *l.c.*; Tommasi, Bull. Soc. chim. 1873, [iii], 20, 20).

**Reactions.**—Nitration converts *acet-a-naphthalide* into a mixture of 2-nitro- and 4-nitro-*acet-a-naphthalide* and finally into 2:4-dinitro-*acet-a-naphthalide*. By sulphonation with warm 20–25% anhydro-acid it yields chiefly *acet-a-naphthalide-5-sulphonic acid*, the 4-sulphonic acid being the minor product, but with 35% anhydro-acid below 30° the 5:7-disulphonic acid is obtained. In acetic acid solution with chlorine it gives 2:4-dichloro-*acet-a-naphthalide* (Cleve, Ber. 1887, 20, 448), but with sodium chlorate and hydrochloric acid 4-chloro-*acet-a-naphthalide* (Reverdin and Crépieux, *ibid.* 1900, 33, 682).

**N-chloroacet-*a*-naphthalide**, dissolved in aqueous alcohol or acetic acid, is changed in the presence of hydrochloric acid to 4-chloro-*acet-a-*

*naphthalide* as main product, some of the 2-chloro-compound being also formed (Hoogveen, Rec. trav. chim. 1930, 49, 503). The effect of varying the acyl substituent on the yield of the nitration products has been studied by Hodgson and Walker (J.C.S. 1934, 180).

#### Alkyl Derivatives.

**N-Methyl-*a*-naphthylamine**, obtained by boiling a solution of formyl-*a*-naphthylamine in xylene with sodium (1 at.), adding methyl iodide (1 mol.) and saponifying the methyl derivative by dilute sulphuric acid, is an oil, b.p. 293° (Fischer, Annalen, 1895, 286, 159; cf. Landshoff, Ber. 1878, 11, 638).

**Reactions.**—It has been proposed as end component in certain disazo-dyes (cf. Cassella, G.P. 71329). The 4-sulphonic acid can be prepared from *a*-naphthol-4-sulphonic acid by interaction with methylamine and methylamine bisulphite at 150° (Badische, G.P. 121683; B.P. 18726, 1900).

**N-Dimethyl-*a*-naphthylamine**, obtained by heating *a*-naphthylamine hydrochloride with methyl alcohol (2 mol.) during 6–8 hours under pressure at 170°, is an oil, b.p. 272–274°,  $\rho^{20}$  1.0423 (Friedländer and Welmans, Ber. 1888, 21, 3124; cf. Pinnow, *ibid.* 1899, 32, 1406). It is prepared in 70% yield from *a*-naphthylamine and methyl sulphate in presence of caustic soda (Gokhle and Mason, J.C.S. 1930, 1757), or in 90–97% yield by heating *a*-naphthylamine with methyl *p*-toluenesulphonate (2 mol.) at 155–160° (Rodinov and Vedenski, Bull. Soc. chim. 1929, [iv], 45, 121). Its chloro-, nitro-, and nitroso-derivatives have been described; the hydrochloride of the nitroso-derivative decomposes into nitroso-*a*-naphthol and dimethylamine in aqueous or alcoholic solutions.

**Reactions.**—By sulphonation with 95% sulphuric acid at 130° it furnishes *dimethyl-a-naphthylamine-5-sulphonic acid*,  $\text{HA} + \text{H}_2\text{O}$ , sparingly soluble scales, together with an easily soluble isomer (Fussgänger, Ber. 1902, 35, 977; cf. Friedländer and Welmans, *l.c.*). Reduction in boiling amyl alcohol solution by sodium converts it into *ar*-tetrahydrodimethyl-*a*-naphthylamine.

**N-Ethyl-*a*-naphthylamine** is an oil, b.p. 303°/722.5 mm. (Friedländer and Welmans, *l.c.*), 325–330°/776 mm., and 191°/16 mm. (Morgan and Micklethwait, J.C.S. 1907, 91, 1516), which, on reduction in boiling amyl alcohol solution with sodium, furnishes *ar*-tetrahydroethyl-*a*-naphthylamine. It is used in the manufacture of Victoria Blue R.

**N-Diethyl-*a*-naphthylamine**, obtained by heating *a*-naphthylamine with caustic soda (2 mol.), a little water, and ethyl bromide or iodide (2 mol.) at 110–120°, and separated easily from the quaternary compound, m.p. 98–100°, also formed, is an oil, b.p. 283–285°,  $\rho$  1.005 (Friedländer and Welmans, *l.c.*).

#### Aryl Derivatives.

**N-Phenyl-*a*-naphthylamine** can be obtained by the interaction of *a*-naphthylamine or *a*-naphthol with aniline in presence of suitable catalysts. The generally adopted method is to heat 250 g. *a*-naphthylamine, 300 g. aniline, and

5 g. sulphanilic acid in a pressure vessel for 24 hours at 210–230°, the ammonia formed being released from time to time. The products of reaction are separated by vacuum distillation, aniline and  $\alpha$ -naphthylamine coming over first and then the phenyl- $\alpha$ -naphthylamine at about 224°/12 mm. The product is of good quality, m.p. 53°. Sulphanilic acid as catalyst gives a purer product than aniline hydrochloride and moreover is less corrosive, enabling an iron vessel to be used (Fierz-David and Blangey, *Farben-Chem.* 1938, Springer, 4th ed.). Alternative catalysts for this reaction are iodine (Knoll, G.P. 241853; Knoevenagel, J. pr. Chem. 1914, [ii], 89, 20) or, preferably, ammonium iodide (Hodgson and Marsden, J.C.S. 1938, 1181). Phenyl- $\alpha$ -naphthylamine has m.p. 62°, b.p. 335°/258 mm. or 226°/15 mm., is insoluble in dilute acids, and couples with diazotised bases as end component in disazo-dyes (cf. Bayer, G.P. 48924; B.P. 14442, 1888). It is used in the manufacture of Victoria Blue B and has found application as an antiager in rubber.

*N*-o-Tolyl- $\alpha$ -naphthylamine, obtained by using *o*-toluidine instead of aniline in the foregoing methods, forms needles, m.p. 94–95°, b.p. 198–202°/9 mm. (Friedländer, l.c.; Knoll, l.c.).

*N*-p-Tolyl- $\alpha$ -naphthylamine, obtained similarly by the use of *p*-toluidine, has m.p. 78–79°, b.p. 360°/258 mm., or 236°/15 mm. (Girard and Vogt, Bull. Soc. chim., 1872, [ii], 18, 68; Friedländer, l.c.; Knoll, l.c.). It couples with diazotised bases as end component in disazo-dyes (cf. Bayer, G.P. 49808; B.P. 14442, 1888).

#### *Aryl- $\alpha$ -naphthylaminesulphonic Acids.*

Of these derivatives, the phenyl- (or *o*- or *p*-tolyl-) 3-, 4-, 5-, 6-, 7-, and 8-sulphonic acids have been prepared by heating the corresponding  $\alpha$ -naphthylaminesulphonic acids with aniline (or *o*- or *p*-toluidine) and its hydrochloride at 160–170°. The acids are very sparingly soluble in water; the sodium salts crystallise in scales, and, with the exception of the 3-, 7-, and 8-sulphonates, are sparingly soluble (Bayer, G.P. 70349; 71158; 71168; B.P. 7337A, 1892). The most important technically are *phenyl*- and *p*-tolyl- $\alpha$ -naphthylamine-8-sulphonic acids used in manufacture of disazo black and navy blue dyes for wool.

Among the  $\alpha$ -naphthylamine-di- and -tri-sulphonic acids, arylation has been confined for the most part to those which contain one of the sulphonic groups in the same nucleus as, and in either the 3- or 4-position relatively to, the amino-group. With these acids:

(a) If the sulphonic group is present in the 4-position, it can be exchanged for hydrogen. Thus the  $\alpha$ -naphthylamine-4:6-, 4:7-, and 4:8-disulphonic acids by arylation furnish respectively the *phenyl* (or *o*- or *p*-tolyl)- $\alpha$ -naphthylamine-6-, 7-, and 8-monosulphonic acids (Aktienges., G.P. 158923; 159353; B.P. 15624, 24669, 1904).

(b) If the sulphonic group is present in the 3-position, it can be exchanged for an arylated amino-group. Thus the  $\alpha$ -

naphthylamine-3:6-, -3:7-, and -3:8-disulphonic acids by arylation yield respectively the *diphenyl*- (or *di-o*- or *di-p*-tolyl)-1:3-diaminonaphthalene-6-, -7-, and -8-monosulphonic acids (Bayer, G.P. 75296; 76414; B.P. 8898, 1893).

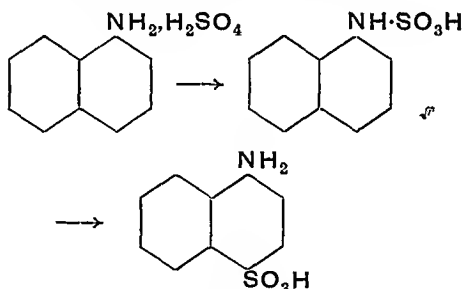
#### $\alpha$ -NAPHTHYLAMINESULPHONIC ACIDS.

$\alpha$ -Naphthylaminesulphonic acids can be prepared by the following general methods, of which the last two are technically unimportant:

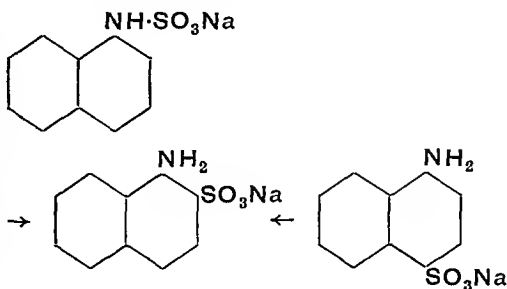
1. By sulphonation of  $\alpha$ -naphthylamine.
2. By nitration of naphthalenesulphonic acids and subsequent reduction.
3. By sulphonation of  $\alpha$ -naphthylaminesulphonic acids obtained from nitronaphthalenesulphonic acids.
4. By heating  $\alpha$ -naphtholsulphonic acids, other than those which contain sulphonic acid groups in the 2- or 3-position, with ammonium sulphite solution and ammonia at 100–150°, and afterwards acidifying the products.
5. By heating  $\alpha$ -chloronaphthalenesulphonic acids with ammonia under pressure.
6. By partial hydrolysis of  $\alpha$ -naphthylamine-di- or -tri-sulphonic acids.

Two of the monosulphonic acids are obtained by methods applicable only to them:

(a)  $\alpha$ -Naphthylamine-4-sulphonic acid, one of the three monosulphonic acids formed from  $\alpha$ -naphthylamine by sulphonation, is obtained mixed only with a small amount of the 5-sulphonic acid by "baking" the acid sulphate of  $\alpha$ -naphthylamine at 180–200°:



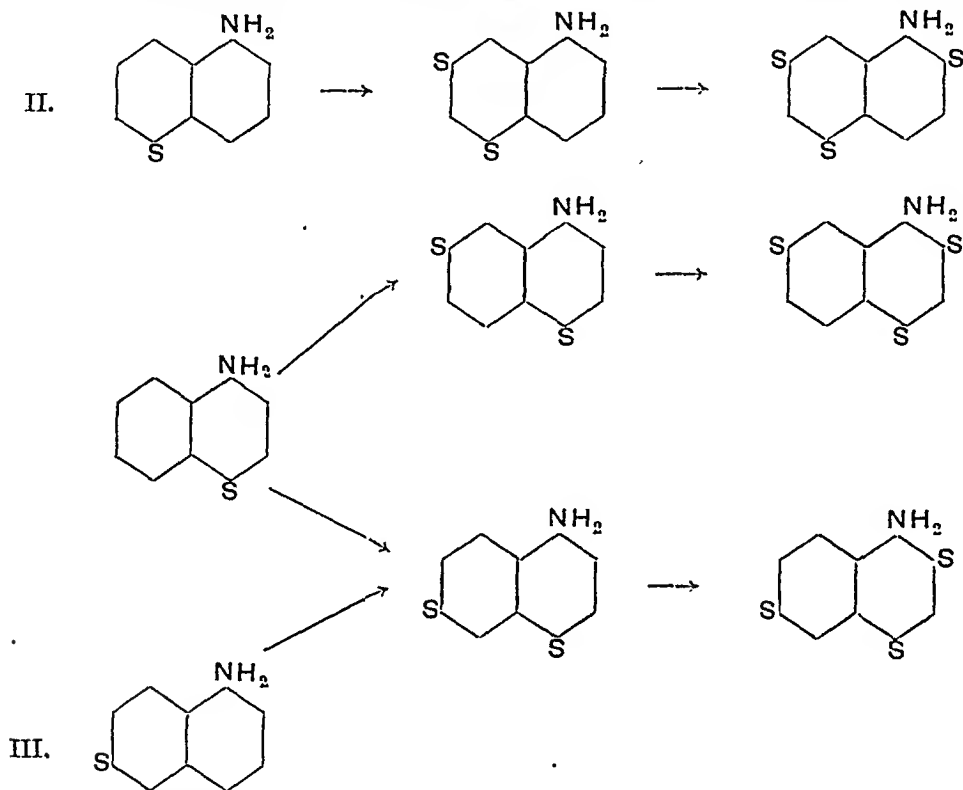
(b)  $\alpha$ -Naphthylamine-2-sulphonic acid is the only monosulphonic acid formed when sodium  $\alpha$ -naphthylsulphamate or sodium  $\alpha$ -naphthylamine-4-sulphonate is heated at about 200°:



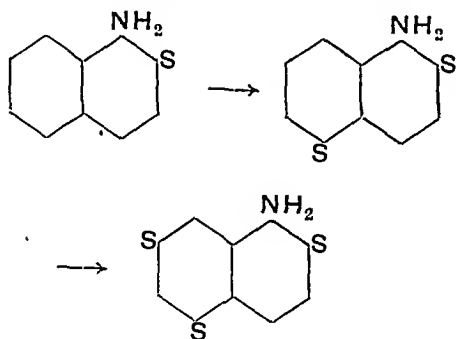
The first general method, the sulphonation of  $\alpha$ -naphthylamine, leads to the formation of three mono-, three di-, and three tri-sulphonic acids. The composition of the sulphonation product depends on the four factors, concentration and relative quantity of the sulphuric acid, and temperature and duration of the reaction; but Erdmann has shown that it is possible to obtain, as chief product, successively the 4-, 5-, and 6-monosulphonic acid by prolonging the reaction without altering the temperature or the

concentration of the sulphuric acid (Annalen, 1893, 275, 192). From the scheme which indicates the constitution of the products obtained by sulphonating each of these three acids it will be seen

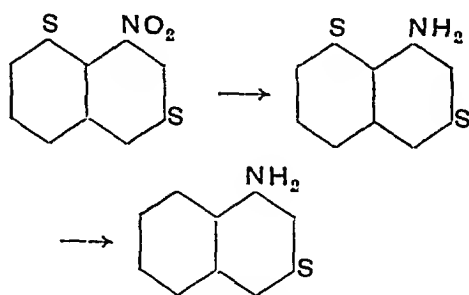
1. that the 2-position is not occupied in acids I, II, and III until trisulphonation occurs;
2. that entry of the sulphonic group into the 3- or the 8-position does not take place:



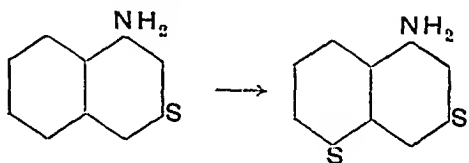
Although in the sulphonation of  $\alpha$ -naphthylamine, its entry into the molecule is delayed until trisulphonation occurs, yet if introduced early (see *supra*) the 2-sulphonic group is retained in position when  $\alpha$ -naphthylamine-2-sulphonic acid interacts with sulphuric acid



reduced in weak acid solution by iron, and in turn these acids by sulphonation or desulphonation may furnish  $\alpha$ -naphthylamino sulphonic acids not obtainable in other ways. Thus the 3-sulphonic acid, like the 3:8-disulphonic acid, arises from  $\alpha$ -nitronaphthalene-3:8-disulphonic acid



and can be further sulphonated

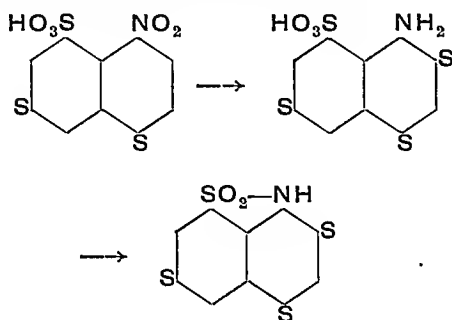


The second and third general methods afford a means whereby several of the more important acids, those containing a sulphonic group in the 8- or *peri*-position, can be obtained. For the production of such acids, nitronaphthalenesulphonic acids of corresponding constitution are

The limit of sulphonation is reached for most of the  $\alpha$ -naphthylaminesulphonic acids when trisulphonation has been effected. Two exceptions only have been observed to this rule and in each the trisulphonic acid which undergoes further sulphonation

- (a) is prepared, not from  $\alpha$ -naphthylamine, but by reduction of the corresponding  $\alpha$ -nitronaphthalene-3:6:8- or 4:6:8-trisulphonic acid, and
- (b) contains one sulphonic-group in the *peri*- or 8-position relatively to the amino radical.

The tetrasulphonation product from either source is isolated from the sulphonation melt as a naphthasultamtrisulphonic acid:



owing to the formation of the *peri*-anhydride or sultam, dehydration in the *peri*-position being a property which characterises both tri- and tetrasulphonic acids of this type.

From solutions of the alkali monosulphonates the acids are precipitated, but from those of the di- and tri-sulphonates, acid salts separate on the addition of mineral acid. A comparison of the relative strengths of the monosulphonic acids shows that the 2-acid is about 10 times as strong as the 4-, 5-, 6-, or 7-acid and about 2,000 times as strong as the 8-acid (Erdmann, *ibid.* 1893, 275, 276).

Naphthylaminesulphonic acids do not form arylamine salts owing probably to internal salt formation. If, however, the amino-group is acetylated—best effected in pyridine solution by acetic anhydride—the production of arylamine salts no longer presents difficulty (Forster and Watson, J.S.C.I. 1927, 46, 224r; Forster, Hanson, and Watson, *ibid.* 1928, 47, 155r, Forster and Mosby, *ibid.* 157r).

The naphthylaminesulphonic acids can be converted into sulphonyl chlorides by the action of chlorosulphonic acid (I.G., B.P. 331596) or in some cases after substituting the amino-group (Aktienges, G.P.a. 38511, Höchst, G.P. 292357).

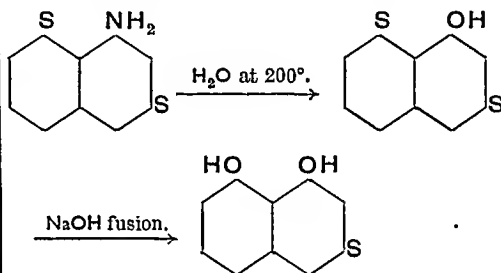
The *naphthylidines* of  $\alpha$ -naphthylamine-4-, 5-, 6-, 7-, and 8-sulphonic acids have m.p. 190°, 171°, 127–128°, 146–147°, and 139–140°, respectively (Heller and Sturm, J. pr. Chem. 1929, [ii], 121, 193).

The rates of diazotisation, of coupling and of decomposition of diazo-compounds of  $\alpha$ -naphthylamine and its seven monosulphonic acids have been measured, from which it appears that

the presence of the sulphonic acid group decreases the stability of the amino-group towards nitrous acid, and that of the acids, the 1:2- and 1:4- are most readily diazotised, 1:5- and 1:8- most tardily (Vendelstein, A. 1927, 760).

A volumetric method for estimating  $\alpha$ - (or  $\beta$ -) naphthylaminesulphonic acids, based on their different capacity for absorbing bromine, has been devised by Vaubel (Chem.-Ztg. 1893, 17, 1265). Most of these acids can be estimated accurately by titration with diazotised *p*-nitraniline (Bucherer, *cf.* J.S.C.I. 1907, 26, 818).  $\alpha$ -Naphthylaminesulphonic acids are used for the following purposes:

(i) *Conversion into  $\alpha$ -Naphtholsulphonic Acids.*—The exchange of amino- for hydroxyl is effected not only by the diazo-reaction or by the bisulphite method but in certain cases by heating the acids with water at 180–200° under pressure. This reaction takes place most readily when sulphonic groups are present in the same nucleus as, or in the 8-position relative to, the amino-group, and, as the example shows, the amino-group is replaced more readily than the  $\alpha$ -sulphonic group by hydroxyl,

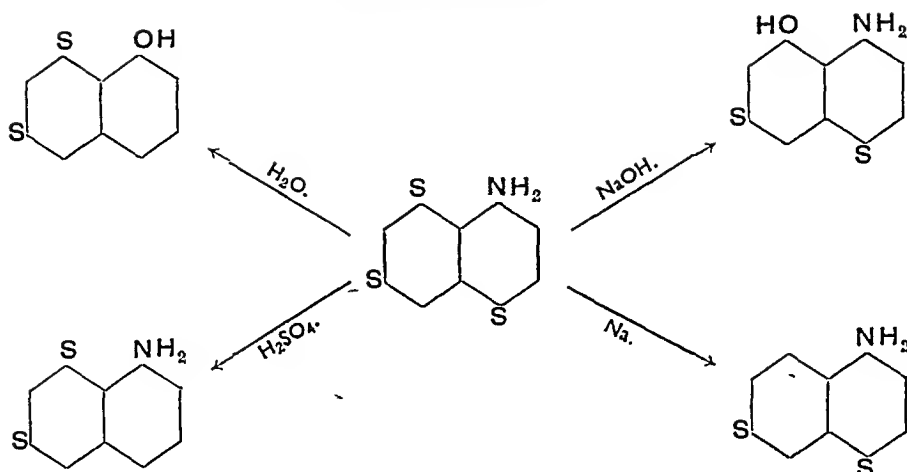


An example of the use of bisulphite is the preparation of  $\alpha$ -naphthol-4-sulphonic acid from naphthionic acid (*see* p. 334b).

(ii) *Conversion into  $\alpha$ -Aminonaphtholsulphonic Acids.*—The exchange of sulphonic for hydroxyl is achieved either by digestion of the sulphonic acid with concentrated caustic soda solution at 180–250° under pressure or by fusion with caustic soda at 180–250°. As is customary, sulphonic groups in  $\alpha$ - are more easily replaced than those in  $\beta$ -positions, and of groups in  $\alpha$ -positions, when there is a choice, that in the 8-position is the first to be exchanged. Acids containing a 3-sulphonic group are decomposed by caustic soda at high temperatures furnishing hydroxy-toluic acids.

(iii) *Conversion into  $\alpha$ -Naphthylaminesulphonic Acids Containing a Smaller Number of Sulphonic Groups.*—The exchange of sulphonic for hydrogen is accomplished by the aid of sodium amalgam in the cold, or of zinc dust in boiling dilute caustic soda solution, or of boiling 75% sulphuric acid. Groups in  $\alpha$ -positions are the first to be eliminated. While the 8-sulphonic group is removed most readily by the first two of these desulphonating agents, hydrolysis by means of sulphuric acid leads preferentially to the elimination of the 4-sulphonic group.

The reactions summarised in the three preceding paragraphs may be illustrated in the case of  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid:

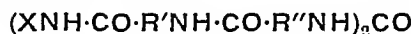


It may be noted that the  $\alpha$ -naphthylamine-4:6-, 4:7-, and 4:8-disulphonic acids when heated with aniline or *p*-toluidine at  $180^\circ$ , furnish aryl- $\alpha$ -naphthylaminemonosulphonic acids by elimination of the 4-sulphonic group.

(iv) *Conversion into Diaminonaphthalenesulphonic Acids*.—The exchange of sulphonic for amino- takes place only when the acid contains a 3-sulphonic group, the 1:3-diaminonaphthalene derivative being produced by interaction of the acid with ammonia at  $180^\circ$ . Aniline and *p*-toluidine furnish 1:3-diaryl-derivatives under these conditions.

(v) *Production of Azo-dyes*.—Diazotisation of the sulphonic acids proceeds normally, except in the case of  $\alpha$ -naphthylamine-2-sulphonic acids which, as already indicated, yield diazo-oxides by exchange of the 2-sulphonic group for hydroxyl in the absence of mineral acid. For an account of the coupling of  $\alpha$ -naphthylamine-sulphonic acids with diazo-compounds, see p. 272b.

(vi) *Formation of Carbamides*.— $\alpha$ -Naphthylaminesulphonic acids, particularly the 4:6:8-trisulphonic acid, have found application in the preparation of trypanocidal substances for combating sleeping sickness. These are compounds of the type



where  $\text{R}'$  and  $\text{R}''$  are phenylene residues and  $\text{X}$  is sulphonated naphthalene (see Bayer, G.P. 228273; 289107; 289270; 289272).

$\alpha$ -Naphthylsulphamic Acid ( $\alpha$ -naphthylamine-*N*-sulphonic acid).—This acid is formed (with naphthionic acid) by ammonium sulphite reduction of  $\alpha$ -nitronaphthalene, from  $\alpha$ -naphthylamine and sulphamic acid at  $110$ – $113^\circ$  (Ruijter de Wildt, Rec. trav. chim. 1904, 23, 183; Quilico, Gazzetta, 1926, 56, 620) or from  $\alpha$ -naphthylamine and chlorosulphonic acid (Tobias, G.P. 79132). The free acid has not been isolated but the alkali salts are soluble and moderately stable in presence of free alkali. When heated the salts are converted to 1-naphthylamine-4-sulphonates (low temperature) or 1-naphthylamine-2-sulphonates (high temperature) (Ruijter de Wildt, l.c.).  $\alpha$ -Naphthylsulphamic acid is easily diazotised (Traube, Ber. 1891, 24, 360; cf. I.G., B.P. 268789). It has been patented for use as the middle component

in polyazo-dyes as it is said to couple exclusively in the *para*-position, whereas  $\alpha$ -naphthylamine couples to some extent in the *ortho*-position as well.

#### $\alpha$ -NAPHTHYLAMINEMONOSULPHONIC ACIDS.

(i)  $\alpha$ -Naphthylamine-2-sulphonic Acid is obtained by heating sodium  $\alpha$ -naphthylamine-4-sulphonate (sodium naphthionate) at  $200$ – $250^\circ$ , but owing to the imperfect distribution of heat throughout the mass, the yield does not exceed 50% (Landshoff, G.P. 56563; B.P. 6195, 1890; cf. Erdmann, Annalen, 1893, 275, 225). If, however, the sodium naphthionate, suspended in boiling naphthalene, be heated at  $180$ – $230^\circ$  for 2–3 hours, and the naphthalene afterwards removed by distillation with steam, the yield is almost quantitative, and the product contains as impurity only a small quantity of  $\alpha$ -naphthylamine (Bayer, G.P. 72833). This acid is also formed when  $\alpha$ -naphthylamine is heated with sulphanilic acid or its homologues at  $180$ – $250^\circ$  (Bayer, G.P. 75319); or with  $\alpha$ -naphthylamine-4- or  $\beta$ -naphthylamine-8-sulphonic acid at  $160$ – $230^\circ$  (Bayer, G.P. 77118; B.P. 21139, 1892); or when  $\alpha$ -naphthylsulphamic acid is heated at  $170$ – $240^\circ$  (Tobias, G.P. 79132; B.P. 15067, 1894).

It is also stated to be obtained from  $\alpha$ -naphthylamine in an indifferent solvent such as tetrachloroethane by the addition of chlorosulphonic acid and subsequent heating for several hours at the boiling-point of the solvent (B.D.C., G.P. 392460).

*Identification*.—The acid crystallises in needles, soluble in 244 parts of water at  $20^\circ$ , or in 31.3 parts at  $100^\circ$  (Dolinski, Ber. 1905, 38, 1836). The barium,  $\text{BaA}_2 + \text{H}_2\text{O}$ , and calcium,  $\text{CaA}_2$ , salts form sparingly soluble scales; the potassium salt,  $\text{KA}$ , needles sparingly soluble in cold water; the sodium salt,  $\text{NaA}$ , scales soluble in 10 parts of boiling or 60 parts of cold water. It is convertible into  $\alpha$ -chloronaphthalene-2-sulphonyl chloride, needles, m.p.  $80^\circ$ , and 1:2-dichloronaphthalene (Cleve, *ibid.* 1891, 24, 3472).

*Reactions*.—From its sparingly soluble diazo-compound,  $\alpha$ -naphthol-2-sulphonic acid has been obtained. Nitration converts it into 5-nitro- $\alpha$ -naphthylamine-2-sulphonic acid. On sulphonation with 10% anhydro-acid in the cold it yields  $\alpha$ -naphthylamine-2:5-disulphonic acid.



(ii) *α*-Naphthylamine-3-sulphonic Acid (*Cleve's [γ]-acid*) can be obtained by the reduction of *α*-nitronaphthalene-3-sulphonic acid with ferrous sulphate (Cleve, Ber. 1886, 19, 2181). It is also formed when sodium *α*-naphthylamine-3:8-disulphonate is boiled with 75% sulphuric acid (Kalle, G.P. 64979), or with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934), or is reduced either by sodium amalgam in the cold (Friedländer and Lucht, Ber. 1893, 26, 3032; Bayer, G.P. 255724; B.P. 28172, 1911) or electrolytically (Bayer, G.P. 248527; 251099; B.P. 28173, 1911).

*Identification*.—The acid forms sparingly soluble needles; the barium salt,  $\text{BaA}_2 + \text{H}_2\text{O}$ , forms scales and, like the calcium, potassium, and sodium, NaA, salts, is very soluble in water (Cleve, Ber. 1888, 21, 3271). It is convertible into *α*-chloronaphthalene-3-sulphonyl chloride, prisms, m.p. 106°, and 1:3-dichloronaphthalene (Cleve, l.c.; Armstrong and Wynne, Proc. C.S. 1895, 11, 240).

*Reactions*.—It couples with diazotised bases as the middle component of disazo-dyes, but has been little used for this purpose. From its diazo-compound *α*-naphthol-3-sulphonic acid has been obtained. Fusion with caustic alkali at 250–260° gives 1-amino-3-naphthol. Digestion with 60% caustic soda solution at 250–280° furnishes *o*-toluic acid (Kalle, G.P. 79028), but with ammonia at 180° gives 1:3-diaminonaphthalene or with aniline at 170° diphenyl-1:3-diaminonaphthalene. By sulphonation with 20% anhydro-acid in the cold, it yields *α*-naphthylamine-3:5-disulphonic acid.

(iii) *α*-Naphthylamine-4-sulphonic Acid (*Naphthionic acid*), was first obtained by boiling *α*-nitronaphthalene with ammonium sulphite in alcoholic solution (Piria, Annalen, 1851, 78, 31). By using pressure, alcohol can be omitted (Ehrhardt and Hereward, B.P. 254402). It is formed when *α*-naphthylamine is sulphonated with "fuming" sulphuric acid (cf. Erdmann, Annalen, 1888, 247, 315), and constitutes the sole product when it is heated with sulphuric acid at 100–130° until the product is soluble in alkali (Witt, Ber. 1886, 19, 57, 578; cf. Verein, B.P. 2237, 1883) or with chlorosulphonic acid (Corbellini, A. 1927, 1179). It is manufactured from acid *α*-naphthylamine sulphate by the "baking" process at 180–200°, preferably in a vacuum (Neville and Winther, J.C.S. 1880, 37, 632; Verein, l.c.; Paul, Z. angew. Chem. 1896, 9, 685). It is also produced by heating *α*-naphthylamine with 3 times its weight of potassium bisulphate at 200° (Bischoff and Brodsky, Ber. 1890, 23, 1914). *α*-Naphthylamine sulphate can also be "baked" with sodium sulphate (Langguth, Chim. et Ind. 1930, 24, 31) or alternatively can be heated in a solvent such as transformer oil, the water of reaction being distilled off (I.C.I., B.P. 354201). It is also formed from *α*-naphthylamine-4:8-disulphonic acid by reduction with zinc dust and boiling dilute caustic soda solution (Kalle, G.P. 233934), or with sodium amalgam in the cold (Bayer, G.P. 255724; B.P. 28172, 1911), or electrolytically (Bayer, G.P. 248527; 251099; B.P. 28173, 1911).

This acid is also the product when the bisul-

phite amination method is applied to sodium *α*-naphthol-4-sulphonate (Badische, G.P. 117471; B.P. 1387, 1900); or when sodium *α*-chloronaphthalene-4-sulphonate is heated with 25% ammonia solution at 200–210° (Oehler, G.P. 72336).

*Preparation*.—Fused *α*-naphthylamine (50 kg.) is stirred into sulphuric acid (36.5 kg.) and the mixture heated at 170–180° until a homogeneous mass is obtained. Crystallised oxalic acid (2.5 kg.) is then stirred in, and the frothy mass, spread on leaden trays, is heated in an oven at 170–180° during 8 hours. When cold, the porous grey product is ground to a powder, extracted by alkali and filtered, the filtrate acidified with hydrochloric acid and the washed precipitate converted into sodium salt (64 kg.). Should the salt still contain *α*-naphthylamine or the 5-sulphonate, the former may be extracted by solvent naphtha, and the latter removed by fractional crystallisation (cf. Schultz, "Chem. d. Steinkohlenth.," F. Wieweg u. Sohn, 3rd ed. i, 202). In a more modern method, *α*-naphthylamine sulphate is baked at a controlled temperature in a rotating cylindrical drum.

*Identification*.—The acid,  $\text{HA} + \frac{1}{2}\text{H}_2\text{O}$ , forms small lustrous needles, which dissolve in 3,225 parts of water at 20°, or in 438 parts at 100° (Dolinski, Ber. 1905, 38, 1836). The barium salt,  $\text{BaA}_2 + 8\text{H}_2\text{O}$ , scales, calcium salt,  $\text{CaA}_2 + 8\text{H}_2\text{O}$ , monodinic tables, potassium salt, KA, scales, and sodium salt dissolve readily in water, and, like the acid, show marked blue fluorescence in dilute solution. It is convertible into *α*-chloronaphthalene-4-sulphonyl chloride (q.v.), and 1:4-dichloronaphthalene (Cleve, *ibid.* 1887, 20, 73).

*Reactions*.—Diazotised, it forms the first component of many azo-dyes. It couples with diazotised bases, Congo Red and Benzopurpurin being familiar dyes in which it is used.

From its sparingly soluble, micro-crystalline, yellow diazo-compound, *α*-naphthol-4-sulphonic acid may be obtained. This acid is also the product when the sodium salt is digested either with sodium bisulphite solution at 85–90°, followed by acidification, or with 50% caustic soda solution at 240–260°. With sodium amalgam in the cold it gives *α*-naphthylamine. By sulphonation with 25% anhydro-acid below 30°, it is converted into a mixture of *α*-naphthylamine-4:6- and -4:7-disulphonic acids. Prolonged heating with sulphuric acid at 130° converts it successively into the 5-sulphonic acid and the 6-sulphonic acid, and it is the most easily hydrolysed acid of the three. Its sodium salt, when heated at 200–250°, is converted into sodium *α*-naphthylamine-2-sulphonate. On bromination it yields 2:4-dibromo-*α*-naphthylamine, the 4-sulphonic group being removed and the amino-group unaffected (Heller and others, Z. angew. Chem. 1930, 43, 1132).

Acet-*α*-naphthalide-4-sulphonic acid, the minor product of the sulphonation of acet-*α*-naphthalide with 20–25% anhydro-acid (Schultz, Ber. 1887, 20, 3161; see the 5-sulphonic acid), is obtained as sodium salt by stirring acetic anhydride (7 parts) into a solution of sodium *α*-naphthylamine-4-sulphonate (15 parts) at 60–70°, and salting out the product.

Both the acid and the sodium salt are crystalline and readily soluble in water (Höchst, G.P. 129000; B.P. 17366, 1898; Nietzki and Zübelen, Ber. 1899, 22, 451). Nitration converts it into the 5-nitro-derivative.

(iv)  $\alpha$ -Naphthylamine-5-sulphonic Acid (*Laurent's acid*; *Cleve's* [ $\alpha$ ]-naphthalidinesulphonic acid) is obtained by reduction of  $\alpha$ -nitronaphthalene-5-sulphonic acid (Laurent, Compt. rend. 1850, 31, 538; cf. Cleve, Förhandl. 1875, 9, 13; Bull. Soc. chim. 1875, [ii], 24, 511; Erdmann, Annalen, 1893, 275, 264; Schöllkopf, G.P. 40571; B.P. 15775, 1885). It constitutes the chief, with the 4-sulphonic acid as subsidiary, product, when  $\alpha$ -naphthylamine is warmed with twice its weight of "fuming" sulphuric acid (Cleve, Förhandl. 1876, 7, 39; cf. Schmidt and Schaal, Ber. 1874, 7, 1367; Erdmann, Annalen, 1888, 247, 316); or when  $\alpha$ -naphthylamine hydrochloride is sulphonated in the cold with 20–25% anhydro-acid (Witt, Ber. 1886, 19, 578; Schultz, *ibid.* 1887, 20, 3161; Mauzelius, *ibid.* 3403); or when acet- $\alpha$ -naphthalide is sulphonated with 3–4 times its weight of 20–25% anhydro-acid and the product deacetylated by boiling the melt with water (Lange, *ibid.* 1887, 20, 2940; Ewer and Pick, G.P. 42874; Schultz, *l.c.*), but is the minor product obtained in the manufacture of the 8-sulphonic acid from naphthalene- $\alpha$ -sulphonic acid by nitration and reduction. It is also formed when sodium  $\alpha$ -chloronaphthalene-5-sulphonate is heated with 25% ammonia solution at 200–210° (Oehler, G.P. 72336).

*Preparation.*—It can be readily prepared by nitrating naphthalene- $\alpha$ -sulphonic acid (*see* (vii), *infra*) or by sulphonation of  $\alpha$ -nitronaphthalene. The 1-nitronaphthalene-5-sulphonic acid is less soluble than the accompanying isomers and can be purified by recrystallising either the sodium or calcium salt, the purity being judged by the melting-point of the derived sulphonyl chloride, which should be 113°. The nitro-compound is reduced to the pure  $\alpha$ -naphthylamine-5-sulphonic acid. Commercially this acid is obtained as a by-product from the manufacture of the 1:8-isomer (*infra*).

*Identification.*—The acid crystallises in anhydrous needles, soluble in about 940 parts of cold water. The *barium* salt,  $\text{BaA}_2 + 6\text{H}_2\text{O}$ ; *calcium* salt,  $\text{CaA}_2 + 9\text{H}_2\text{O}$ , tables; *potassium* salt,  $\text{KA} + \text{H}_2\text{O}$ , needles; and *sodium* salt,  $\text{NaA} + \text{H}_2\text{O}$ , aggregates of needles, dissolve readily in water; both acid and salts show greenish fluorescence in dilute aqueous solution (Cleve, Bull. Soc. chim. 1875, [ii], 24, 511; Witt, *l.c.*; Mauzelius, *l.c.*). It is convertible into  $\alpha$ -chloronaphthalene-5-sulphonyl chloride (*q.v.*) and 1:5-dichloronaphthalene (Erdmann, Annalen, 1888, 247, 353).

*Reactions.*—Diazotised, it forms the first component of several azo-dyes. It couples with diazotised *p*-nitraniline, forming both the *ortho*- and the *para*-azo-dye. From its sparingly soluble, yellow, crystalline diazo-compound,  $\alpha$ -naphthol-5-sulphonic acid may be obtained. Digestion with concentrated caustic soda solution at 250° converts it into 1-amino-5-naphthol. By the Bucherer reaction,  $\alpha$ -naphthol-5-sulphonic acid can be obtained in 85% yield (Kogan and

Nikolaeva, J. Appl. Chem. Russia, 1938, 11, 652). By sulphonation with 35% anhydro-acid at 90–120°, it yields  $\alpha$ -naphthylamine-2:5:7-trisulphonic acid, the intermediate 5:7-disulphonic acid being obtained by sulphonation of its acetyl derivative with 30% anhydro-acid in the cold, and subsequent deacetylation. On bromination it gives, besides a non-diazotisable bromo-compound, 2:4-dibromo- $\alpha$ -naphthylamine-5-sulphonic acid (Heller *et al.*, Z. angew. Chem., 1930, 43, 1132).

(v)  $\alpha$ -Naphthylamine-6-sulphonic Acid (*Cleve's* [ $\beta$ ]-acid; *Erdmann's* [ $\mu$ ]-acid), formed when  $\alpha$ -naphthylamine-4-sulphonic acid or 5-sulphonic acid is heated with sulphuric acid at 125–130°, for many hours (Erdmann, Annalen, 1893, 275, 200), is prepared by reduction of  $\alpha$ -nitronaphthalene-6-sulphonic acid by ammonium sulphide or by iron and dilute sulphuric acid (Cleve, Ber. 1887, 20, 74).

*Preparation.*—The product obtained by nitrating naphthalene- $\beta$ -sulphonic acid, which consists almost entirely of a mixture of the  $\alpha$ -nitronaphthalene-6- and -7-sulphonic acids (*q.v.*), after dilution with water, is neutralised by lime and the filtrate, rendered acid by acetic acid in small quantity, reduced at the boiling-point by soft-iron borings. The resulting solution is then freed from iron by milk of lime, concentrated, and either treated with sodium carbonate to obtain the greater part of the 7-isomer as sparingly soluble sodium salt, or the mixed Cleve acids precipitated from the concentrated solution by hydrochloric acid.

For many azo-dyes, mixed 1:6- and 1:7-acids are used. If the pure acids are required, then, according to Fierz-David, enough magnesite is added to the diluted nitration melt to combine with the calculated amount of sulphonic acid present, the excess of sulphuric acid neutralised by lime, and the reduction carried out as just described. When the boiling liquid has become colourless, it is neutralised by the addition of magnesite, and the filtrate after concentration to a small bulk precipitated by hydrochloric acid. The precipitate, 2–3 days later, is collected on a filter (the filtrate being violet owing to the presence of hydroxylamine compounds) and washed with cold water until colourless. As much as 28% of the calculated yield of Cleve acids may be lost in this filtrate. The acids, now free from impurities, isomers, and disulphonic acids, are converted into sodium salts and finely powdered common salt stirred in the hot concentrated solution during one day, to effect a complete separation of the pure sodium 7-sulphonate. From the mother-liquor on acidification, a precipitate of the 6-sulphonic acid in an almost pure state is obtained, the remaining impurity being removable by retreatment (H. E. Fierz-David and L. Blangoy, "Farbenchemie," 4th ed., p. 129).

*Identification.*—The acid,  $\text{HA} + 2\text{H}_2\text{O}$ , forms needles soluble in 1,000 parts of water at 16°. The *barium* salt,  $\text{BaA}_2 + \text{H}_2\text{O}$ , needles, is only sparingly, but the *calcium* salt,  $\text{CaA}_2 + 7\text{H}_2\text{O}$ , tablets, *potassium* salt,  $\text{KA} + \text{H}_2\text{O}$ , scales, and *sodium* salt,  $\text{NaA} + \frac{1}{2}\text{H}_2\text{O}$ , thin tablets, are easily soluble in water (Cleve, Förhandl. 1876, 7, 54; Bull. Soc. chim. 1876, [ii], 26, 447;

Erdmann, *l.c.*, p. 265). It is convertible into *α-chloronaphthalene-6-sulphonyl chloride* (*q.v.*), and 1:6-dichloronaphthalene (Erdmann, *l.c.*).

**Reactions.**—It couples with diazotised bases and is of importance as the middle or end component of disazo or trisazo-dyes. From its diazo-compound or by the bisulphite method, *α-naphthol-6-sulphonic acid* may be obtained. Fusion with caustic alkali converts it into 1-amino-6-naphthol. By sulphonation with 10% anhydro-acid it yields *α-naphthylamine-4:6-disulphonic acid*.

(vi) *α-Naphthylamine-7-sulphonic Acid* (Cleve's [β-] or [δ]-acid; *Cleve's acid*) obtained by the reduction of *α-nitronaphthalene-7-sulphonic acid* (Cleve, *Ber.* 1888, 21, 3264; Erdmann, *Annalen*, 1893, 275, 272), or by boiling *α-naphthylamine-2:7-disulphonic acid* with 80% sulphuric acid (Kalle, G.P. 62634), or from *α-naphthol-7-sulphonic acid* by the bisulphite method (Badische, G.P. 117471; B.P. 1387, 1900).

**Preparation.**—This acid is obtained, mixed with about an equal amount of the 6-sulphonic acid (*q.v.*) by reduction of the nitration product of naphthalene-β-sulphonic acid and easily separated from its isomer owing to the sparing solubility of its sodium salt in brine.

**Identification.**—The acid,  $\text{HA} + \text{H}_2\text{O}$ , forms scales soluble in 220 parts of water at 25°. The barium salt,  $\text{BaA}_2$ , needles, is only sparingly, but the calcium salt,  $\text{CaA}_2 + 2\text{H}_2\text{O}$ , potassium salt, scales, and sodium salt,  $\text{NaA} + \frac{1}{2}\text{H}_2\text{O}$ , needles, are easily soluble in water (Cleve, *l.c.*). It is convertible into *α-chloronaphthalene-7-sulphonyl chloride* (*q.v.*) and 1:7-dichloronaphthalene (Armstrong and Wynne, *Proc. C.S.* 1889, 5, 49).

**Reactions.**—It couples with diazotised bases, and is of much importance as the middle or end component of many disazo- and trisazo-dyes. From its diazo-compound or by the bisulphite method, *α-naphthol-7-sulphonic acid* may be obtained. Digestion with 60% caustic soda solution at 250° converts it into 1-amino-7-naphthol. By sulphonation with 25% anhydro-acid at 50° it yields *α-naphthylamine-4:7-disulphonic acid*.

(vii) *α-Naphthylamine-8-sulphonic Acid* (*Schöllkopf acid*: usually known as *peri-acid*) is obtained by reduction of *α-nitronaphthalene-8-sulphonic acid* in acid solution with iron (Schöllkopf, G.P. 40571; B.P. 15775, 1885); it is also formed when sodium 1:8-naphthasultam-2:4-disulphonate is digested with 20% hydrochloric acid at 150° (Dressel and Kothe, *Ber.* 1894, 27, 2140).

**Preparation.**—Naphthalene is sulphonated to naphthalene-*α*-sulphonic acid by being stirred into sulphuric acid and allowing the temperature to rise not above 55°. The mass is then nitrated to a mixture of *α-nitronaphthalene-5-* and *-8-sulphonic acids* to which, after diluting with water, is added enough magnesium or ammonium sulphate to form the salt of the sulphonic acid and then lime to remove the sulphuric acid as gypsum. The solution of nitronaphthalenesulphonate (magnesium or ammonium salt) is then reduced by making faintly acid, running into a boiling water suspension of

iron borings with ferrous sulphate as catalyst, and precipitating soluble iron by adding the appropriate alkali (magnesia or ammonia). The filtered solution now contains the mixed *α-naphthylamine-8-* and *-5-sulphonic acids* (*peri-* and *Laurent acids* respectively) as soluble salts (the sodium salt of *peri-acid* is too sparingly soluble for this process). The two acids are separated by taking advantage of the fact that on acidification the *peri-acid* is precipitated before the *Laurent acid*. The amount of acid to be added to precipitate only the former can be controlled by pH measurement (Du Pont, U.S.P. 1912639; Tinker, B.P. 389098; Nat. Aniline and Chem. Corp. U.S.P. 1996822). The precipitated *peri-acid* is filtered off and from the filtrate *Laurent acid* is isolated in an impure form by completing the acidification.

**Identification.**—The acid,  $\text{HA} + \text{H}_2\text{O}$ , forms needles soluble in 4,800 parts of water at 21° or in 238 parts of boiling water; the potassium salt,  $\text{KA}$ , scales, soluble in 280 parts of water at 19° or in 67 parts at 100°; the sodium salt,  $\text{NaA}$ , scales or tables, soluble in 885 parts of water at 24° or in 375 parts at 100° (Erdmann, *Annalen*, 1888, 247, 320). It is convertible into *α-chloronaphthalene-8-sulphonyl chloride* (*q.v.*) and 1:8-dichloronaphthalene (Armstrong and Wynne, *Proc. C.S.* 1895, 11, 84).

**Reactions.**—It couples with diazotised bases, and has been used as middle or end component in azo-dyes. From its sparingly soluble diazo-compound naphthasultone (the anhydride of *α-naphthol-8-sulphonic acid*) can be obtained. Digestion with water at 200° converts it into *α-naphthol-8-sulphonic acid*, and with 9% caustic soda solution at 220–260° into 1:8-dihydroxynaphthalene, but fusion with caustic alkali at 200° furnishes 1-amino-8-naphthol. By dehydration with phosphorus oxychloride at 130°, it yields the anhydride, *naphthasultam*, and with 40% anhydro-acid at 80–90° *naphthasultam-2:4-disulphonic acid* is formed, but with 10% anhydro-acid in the cold sulphonation alone occurs, *α-naphthylamine-4:8-disulphonic acid* being the product. If *peri-acid* is stirred with excess of concentrated sulphuric acid for several hours at 75–80° it is converted into naphthionic acid (Wahl and Vermeulen, *Compt. rend.* 1927, 184, 334).

*N-Phenyl-α-naphthylamine-8-sulphonic Acid* (*phenyl-peri-acid*) is obtained when *α-naphthylamine-8-sulphonic acid* (1 part) is heated with aniline (3·5 parts) and aniline hydrochloride (1 part) at 160–170° for 10 hours (Bayer, G.P. 70349; 71168; B.P. 7337A, 1892)—iodine can also be used as catalyst (Hodgson and Marsden, J.S.C.I. 1939, 58, 154–159)—or when the acid sodium salt of *α-naphthylamine-4:8-disulphonic acid* (1 part) is heated with aniline (4 parts) at 180° for 30 hours (Aktienges., G.P. 158923; B.P. 15624, 1904). The product, after being rendered alkaline, is freed from aniline by distillation with steam and the phenylated acid precipitated by hydrochloric acid, or salted out, or used in solution without isolation. The acid is only sparingly, but the sodium salt easily soluble in water. It couples with diazotised bases forming monoazo-dyes. It is used in the important azo-dye Coomassie Navy Blue 2RN.

$\alpha$ -NAPHTHYLAMINEDISULPHONIC ACIDS.

(i)  $\alpha$ -Naphthylamine-2:4-disulphonic Acid is obtained when  $\alpha$ -naphthylamine-2:4:6-trisulphonic acid is reduced electrolytically, or by sodium amalgam (Bayer, G.P. 248527; 251099; 255724; B.P. 28172; 28173, 1911) or, mixed with the 4-sulphonic acid in small amount, when  $\alpha$ -nitronaphthalene is heated with sodium bisulphite solution at 100° (Höchst, G.P. 92082). Its sodium salt is easily soluble in water.

**Reactions.**—Its diazo-compound yields *naphthalene-1:3-disulphonic acid* by elimination of the amino-group, and *2:4-dinitro- $\alpha$ -naphthol* when warmed with dilute nitric acid (Höchst, l.c.). Fused with caustic alkali, it furnishes *1-amino-2-naphthol-4-sulphonic acid*, whilst its diazo-compound, oxidised by hypochlorite in sodium bicarbonate solution, furnishes the diazo-oxide of this acid (Badische, G.P. 160536; B.P. 4997, 1904).

(ii)  $\alpha$ -Naphthylamine-2:5-disulphonic Acid is obtained from  $\alpha$ -naphthylamine-2-sulphonic acid by sulphonation with 10% anhydro-acid in the cold (Landshoff, G.P. 56563; B.P. 6195, 1890). It is easily soluble, but its acid salts are only very sparingly soluble in water.

**Reactions.**—It yields *naphthalene-1:6-disulphonic acid* by elimination of the amino-group, and  *$\alpha$ -naphthylamine-5-sulphonic acid* by partial hydrolysis with dilute sulphuric acid at 160° (Tobias, Ber. 1890, 23, 1631; Landshoff, l.c.). Digestion with 50% caustic soda solution at 240–270° furnishes *1-amino-5-naphthol-2-sulphonic acid*. By sulphonation with 40% anhydro-acid at 120° it is converted into  *$\alpha$ -naphthylamine-2:5:7-trisulphonic acid*.

(iii)  $\alpha$ -Naphthylamine-2:6-disulphonic Acid, stated to be obtained when  $\alpha$ -naphthylamine-2:4:6-trisulphonic acid is heated with mineral acids, has not been described (Bayer, G.P.a. 31910).

(iv)  $\alpha$ -Naphthylamine-2:7-disulphonic Acid, obtained by partial hydrolysis of  $\alpha$ -naphthylamine-2:4:7-trisulphonic acid with water at 230° under pressure (Kalle, G.P. 62634), is also formed when  $\alpha$ -naphthylamine-2:5:7-trisulphonic acid is desulphonated either by sodium amalgam in the cold (Bayer, G.P. 255724; B.P. 28172, 1911) or by boiling it with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934). It crystallises in needles; its *barium* salt is very sparingly soluble in water, and solutions of its alkali salts show bluish-green fluorescence (Kalle, G.P. 62634).

**Reactions.**—It yields  *$\alpha$ -naphthol-2:7-disulphonic acid* by the diazo-reaction, *naphthalene-2:7-disulphonic acid* by elimination of the amino-group, and  *$\alpha$ -naphthylamine-7-sulphonic acid* by heating it with dilute sulphuric acid or water under pressure (Kalle, l.c.).

(v)  $\alpha$ -Naphthylamine-2:8-disulphonic Acid is obtained from *naphthasultam-2:4-disulphonic acid* by partial hydrolysis with 40% sulphuric acid at 110° (Cassella, G.P. 75710). It crystallises in moderately soluble long needles; the solutions of its alkali salts show green fluorescence.

**Reactions.**—With nitrous acid (1 mol.) it does not give a reactive diazo-compound, but it

couples with diazotised bases forming azo-dyes. Fusion with caustic soda converts it into *1-amino-8-naphthol-2-sulphonic acid*.

(vi)  $\alpha$ -Naphthylamine-3:5-disulphonic Acid is formed by sulphonating  $\alpha$ -naphthylamine-3-sulphonic acid with 4 times its weight of 20% anhydro-acid in the cold.

**Identification.**—The *acid potassium* salt,  $KHA+2H_2O$ , forms short needles convertible into  *$\alpha$ -chloronaphthalene-3:5-disulphonyl chloride*, m.p. 130°, and *1:3:5-trichloronaphthalene* (Armstrong and Wynne, Proc. C.S. 1895, 11, 240).

(vii)  $\alpha$ -Naphthylamine-3:6-disulphonic Acid (*Alén's [a]-acid*; *Freund's acid*) is obtained by reduction of  $\alpha$ -nitronaphthalene-3:6-disulphonic acid (Alén, Förhandl. 1883, 8, 3; Freund, G.P. 27346; B.P. 1069, 1883; Armstrong and Wynne, Proc. C.S. 1895, 11, 82), or by boiling  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934; Ostroslinskaja, Anilinokras Prom. 1935, 5, 138–143).

**Preparation.**—The nitration product of sodium naphthalene-2:7-disulphonate diluted with water is reduced by soft-iron borings, the iron and excess of sulphuric acid removed by lime, and the filtrate, after precipitation by sodium carbonate, acidified and evaporated to obtain the acid sodium salt.

**Identification.**—The acid forms needles, and, like the *barium*,  $BaA+4H_2O$ , and *calcium*,  $CaA+5H_2O$ , tablets, also the *acid potassium*,  $KHA+3H_2O$ , and *acid sodium*,  $NaHA+3H_2O$  salts, needles, is easily soluble in water (Alén, l.c.). It is convertible into  *$\alpha$ -chloronaphthalene-3:6-disulphonyl chloride*, and *1:3:6-trichloronaphthalene* (Armstrong and Wynne, l.c.).

**Reactions.**—From its diazo-compound,  *$\alpha$ -naphthol-3:6-disulphonic acid* can be obtained. This acid is also formed when it is digested with water at 180°, but when it is boiled with 75% caustic potash solution the product is a mixture of the *1-amino-3-naphthol-6-sulphonic* and *1-amino-6-naphthol-3-sulphonic acids*. Digestion with ammonia at 180° converts it into *1:3-diaminonaphthalene-6-sulphonic acid*, and with aniline (or *p*-toluidine) at 150–160° into *diphenyl* (or *di-p-tolyl*)-*1:3-diaminonaphthalene-6-sulphonic acid*.

It has been used for the preparation of trypanocidal substances (Bayer, G.P. 288273).

(viii)  $\alpha$ -Naphthylamine-3:7-disulphonic Acid (*Alén's [β]-acid*), prepared by reduction of  $\alpha$ -nitronaphthalene-3:7-disulphonic acid (Freund, G.P. 27346; B.P. 1069, 1883; Cassella, G.P. 57007; 58352; Levinstein, B.P. 2682, 1891) is also formed when  $\alpha$ -naphthylamine-3:5:7-trisulphonic acid is desulphonated either by sodium amalgam in the cold (Bayer, G.P. 255724; B.P. 28172, 1911) or by boiling it with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934).

**Identification.**—It is easily soluble in water, and, like its salts, shows blue fluorescence in solution. The *barium* salt,  $BaA+H_2O$ , *calcium* salt,  $CaA+2H_2O$ , and *acid potassium* salt,  $KHA$ , form sparingly soluble needles (Alén, Förhandl. 1883, 8, 26).

**Reactions.**—From its diazo-compound  *$\alpha$ -naphthol-3:7-disulphonic acid* can be obtained. This acid is also formed when it is digested with

water at 180°, but with 40% caustic soda solution at 200° the product is a mixture of 1-amino-7-naphthol-3-sulphonic acid with an isomeric acid (Cassella, G.P. 57007). Digestion with ammonia at 180° converts it into 1:3-diaminonaphthalene-7-sulphonic acid, and with aniline (or *p*-toluidine) at 150–160° into diphenyl-(or di-*p*-tolyl)-1:3-diaminonaphthalene-7-sulphonic acid.

(ix)  $\alpha$ -Naphthylamine-3:8-disulphonic Acid ( $[\epsilon$ -acid) is obtained by reduction of  $\alpha$ -nitronaphthalene-3:8-disulphonic acid in acid solution at the boiling-point by iron borings or on the small scale by zinc dust (cf. Paul, Z. angew. Chem. 1896, 9, 562).

**Preparation.**—The mixture of this acid with  $\alpha$ -nitronaphthalene-4:8-disulphonic acid, and some  $\beta$ -nitronaphthalenedisulphonic acids, obtained by nitrating a disulphonation melt containing the naphthalene-1:5- and -1:6-disulphonic acids, is diluted with water, neutralised by lime, acidified slightly by sulphuric acid, reduced hot by soft-iron borings, again neutralised by lime and the filtrate converted into sodium salt. After concentration of the filtrate to a small bulk, the 4:8-disulphonic acid separates from the solution in the course of several days as the normal sodium salt, the more soluble 3:8-salt being retained in the mother-liquor from which it is precipitated as acid sodium salt by the addition of hydrochloric acid. The final mother-liquor contains the highly soluble sodium  $\beta$ -naphthylaminedisulphonates (Aktienges., G.P. 45776; B.P. 4625, 1888; Ewer and Pick, G.P. 52724; Bernthsen, Ber. 1889, 22, 3328; Schultz, *ibid.* 1890, 23, 77). The separation may be achieved in the same way with the barium salts but more rapidly, as hot solutions may be used (S. Metro. Gas Co. and Stanier, B.P. 161859).

**Identification.**—The acid,  $H_2A + 3H_2O$ , forms very soluble scales. The barium salt,  $BaA + 4H_2O$ , forms needles sparingly soluble, and the acid barium salt,  $BaH_2A_2 + 5H_2O$ , microscopic needles almost insoluble in cold water; the normal sodium salt,  $Na_2A + 5H_2O$ , very soluble, and the acid sodium salt,  $NaHA + 2H_2O$ , soluble in about 30 parts of cold water, crystallise in long needles or thin prisms (Bernthsen, *l.c.*). It is convertible into  $\alpha$ -chloronaphthalene-3:8-disulphonyl chloride (*q.v.*) and 1:3-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 16).

**Reactions.**—It couples with diazotised *m*- or *p*-nitroaniline (Aktienges., G.P. 170513; 174548), but not with diazotised aniline (cf. Bayer, G.P. 75084). From the diazo-compound, naphthasultone-3-sulphonic acid, but by prolonged boiling with dilute sulphuric acid  $\alpha$ -naphthol-3:8-disulphonic acid is obtained. This disulphonic acid is also formed when  $\alpha$ -naphthylamine-3:8-disulphonic acid is digested with water at 180°; desulphonation, however, occurs, and  $\alpha$ -naphthylamine-3-sulphonic acid is the product when it is boiled with 75% sulphuric acid, or with zinc dust and dilute caustic soda solution, or is acted on by sodium amalgam in the cold.

Fusion with caustic alkali below 210° furnishes 1-amino-8-naphthol-3-sulphonic acid, but when it is heated with 9% caustic soda solution at 250° it yields 1:8-dihydroxynaphthalene-3-sul-

phonic acid. Digestion with ammonia at 180° converts it into 1:3-diaminonaphthalene-8-sulphonic acid and with aniline (or *p*-toluidine) at 150–160° into diphenyl-(or di-*p*-tolyl)-1:3-diaminonaphthalene-8-sulphonic acid. When sulphonated with 40% anhydro-acid at 80–90°, naphthasultamdisulphonic acid- $\epsilon$  is the product.

(x)  $\alpha$ -Naphthylamine-4:6-disulphonic Acid (*Dahl's No. II acid*) constitutes about 30% of the product obtained by sulphonating  $\alpha$ -naphthylamine-4-sulphonic acid with 25% anhydro-acid in the cold (see the 4:7-disulphonic acid), and is separated by extraction of the mixed calcium salts with 85% alcohol in which it is soluble (Dahl, G.P. 41597).

It is formed when  $\alpha$ -naphthylamine-6-sulphonic acid is sulphonated with 10% (Cassella, G.P.a. 4021) or 25% anhydro-acid (Bayer, G.P.a. 7016; B.P. 15223, 1893) or when  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid is boiled for some hours with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934), or when the bisulphite method of amination is applied to  $\alpha$ -naphthol-4:6-disulphonic acid (Badische, G.P. 117471; B.P. 1387, 1900).

**Identification.**—The calcium salt,  $CaA + 5H_2O$ , forms needles soluble in 85% but insoluble in 96% alcohol (Erdmann, Annalen, 1893, 275, 219), and, like the potassium and sodium salts, is very soluble in water; the acid sodium salt, needles, is soluble in about 6 parts of water at 20° (Dahl, *l.c.*). It is convertible into  $\alpha$ -chloronaphthalene-4:6-disulphonyl chloride, m.p. 126–127°, and 1:4:6-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 126).

**Reactions.**—It couples with diazotised bases. From its moderately soluble diazo-compound or by the bisulphite method  $\alpha$ -naphthol-4:6-disulphonic acid can be obtained. Fusion with caustic soda at 180–200° converts it into 1-amino-6-naphthol-4-sulphonic acid, and at 200–220° into 1:6-dihydroxynaphthalene-4-sulphonic acid. Heated with aniline (or *p*-toluidine) at 180°, it forms phenyl-(or *p*-tolyl)- $\alpha$ -naphthylamine-6-sulphonic acid by elimination of the 4-sulphonic group. By sulphonation with 35% anhydro-acid at 80–90°  $\alpha$ -naphthylamine-2:4:6-trisulphonic acid is obtained.

(xi)  $\alpha$ -Naphthylamine-4:7-disulphonic Acid (*Dahl's No. III acid*) is obtained, mixed with about 30% of the No. II acid (see the 4:6-disulphonic acid), by adding sieved  $\alpha$ -naphthylamine-4-sulphonic acid slowly to 3.5 times its weight of 25% anhydro-acid below 30° and stirring for 2–3 days, or until 6 drops of the melt added to 10 c.c. of water give a solution which remains clear at the end of 6 hours. The product converted into dry calcium salt and powdered is extracted with 10 times its weight of 85% alcohol to remove No. II salt, the residue being No. III salt (Dahl, G.P. 41957).

It is also formed when  $\alpha$ -naphthylamine-7-sulphonic acid is sulphonated with monohydrate at 100–150° (Cassella, G.P.a. 3939), or 25% anhydro-acid at 50–60° (Bayer, G.P.a. 6550; B.P. 15223, 1893); or when 1:8-dinitronaphthalene is digested with 40% sodium bisulphite solution and 25% ammonia solution at 80–90° for 8 hours, the filtrate stirred with about one-third of its weight of concentrated hydrochloric



acid for half a day to decompose the sulphamino-acids which result, and the separation recrystallised from water in which the 4:7-disulphonic acid is only sparingly, but the 2:4:7-trisulphonic acid so easily soluble as to need salting out from the solution (Höchst, G.P. 215338); or when the bisulphite method of amination is applied to sodium  $\alpha$ -naphthol-4:7-disulphonate (Badische, G.P. 117471; B.P. 1387, 1900).

**Identification.**—The barium salt,  $BaA$ , needles, and calcium salt,  $CaA + H_2O$ , are sparingly soluble in water; the potassium salt,  $K_2A + 3H_2O$ , efflorescent prisms, and sodium salt,  $Na_2A + 3H_2O$ , efflorescent needles, are readily soluble in water; the acid sodium salt, needles, is soluble in 140 parts of water at 20°, or 20 parts at the boiling-point, but like the calcium salt, is insoluble in 85% alcohol (Dahl, l.c.; Erdmann, Annalen, 1893, 275, 220). The solutions of the acid and salts show blue fluorescence. It is convertible into  $\alpha$ -chloronaphthalene-4:7-disulphonyl chloride, m.p. 107°, and 1:4:6-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 17).

**Reactions.**—It couples with diazotised bases. From its diazo-compound or by the bisulphite method,  $\alpha$ -naphthol-4:7-disulphonic acid can be obtained. Heated with aniline (or *p*-toluidine) at 180°, it forms phenyl-(or *p*-tolyl)- $\alpha$ -naphthylamine-7-sulphonic acid by elimination of the 4-sulphonic group. By sulphonation with 35% anhydro-acid at 80–90° it yields  $\alpha$ -naphthylmine-2:4:7-trisulphonic acid.

(xii)  $\alpha$ -Naphthylamine-4:8-disulphonic Acid ([8]-acid; disulpho-acid-S) is formed from  $\alpha$ -naphthylamine-8-sulphonic acid by sulphonation with 3 times its weight of 10% anhydro-acid at first in the cold and afterwards at 100° (Schöllkopf, G.P. 40571; B.P. 15775, 1885); also, mixed with the 6:8-disulphonic acid, when acet- $\alpha$ -naphthalide-8-sulphonic acid is sulphonated with 25% anhydro-acid in the cold, the product deacetylated by boiling with water, and the sodium salt separated from the more soluble 6:8-isomer by fractional crystallisation (Bayer, G.P. 75084). From the  $\alpha$ -naphthol-4:8-disulphonic acid it can be obtained by the bisulphite amination method (Badische, G.P. 117471; B.P. 1387, 1900).

**Preparation.**—It is obtained by reduction of  $\alpha$ -nitronaphthalene-4:8-disulphonic acid, and is present therefore, with the 3:8-disulphonic acid (*q.v.*), in the product formed when the sulphonation melt containing naphthalene-1:5- and 1:6-disulphonic acids is nitrated, and the nitro-acids are reduced (Aktienges., G.P. 45776; B.P. 4625, 1888; Bernthsen, Ber. 1889, 22, 3327; Paul, Z. angew. Chem. 1896, 9, 563).

**Identification.**—The normal sodium salt,  $Na_2A + 2H_2O$ , forms needles readily soluble in water (Bernthsen, Ber. 1890, 23, 3090, footnote); the acid sodium salt scales sparingly soluble in cold water. It is convertible into  $\alpha$ -chloronaphthalene-4:8-disulphonyl chloride (*q.v.*) and 1:4:5-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 126).

**Reactions.**—It couples easily with diazotised bases. From the diazo-compound, or by the bisulphite method,  $\alpha$ -naphthol-4:8-disulphonic acid can be obtained. Fusion with caustic soda

at 200° converts it into the important 1-amino-8-naphthol-4-sulphonic acid, but digestion with 60% caustic soda solution at 250° furnishes 1:8-dihydroxynaphthalene-4-sulphonic acid.

When heated with anilino (or *p*-toluidine) at 180° it yields phenyl-(or *p*-tolyl)- $\alpha$ -naphthylamine-8-sulphonic acid by elimination of the 4-sulphonic group, but this group is retained and the 8-sulphonic group removed,  $\alpha$ -naphthylamine-4-sulphonic acid being the product, when desulphonation is effected by sodium amalgam in the cold, or by zinc dust and dilute caustic soda solution at the boiling-point. By sulphonation with 40% anhydro-acid, it forms naphthasultam 2:4-disulphonic acid.

(xiii)  $\alpha$ -Naphthylamine-5:7-disulphonic Acid is obtained when  $\alpha$ -naphthylamine-5-sulphonic acid (1 part) after acetylation, is mixed with 30% anhydro-acid (8 parts), or acet- $\alpha$ -naphthalido (1 part) with 35% anhydro-acid (5 parts) at 0–5°; the mixture kept at 20–30° for 15–20 hours until a sample, boiled with water, shows no separation of monosulphonic acid in the cold; and the product, after deacetylation by boiling the melt with water (10 parts), converted into acid sodium salt by saturating the hot solution with common salt (Badische, G.P. 69555). The acid sodium salt,  $NaH_2A_2 + 5H_2O$ , needles, is very soluble but the acid barium salt almost insoluble in cold water.

**Reactions.**—In alkaline solution it couples readily with diazotised bases. From its diazo-compound or by the bisulphite method,  $\alpha$ -naphthol-5:7-disulphonic acid can be obtained. Digestion with 75% caustic soda solution at 170–180° converts it into 1-amino-5-naphthol-7-sulphonic acid. By sulphonation with 40% anhydro-acid at 120–130°, it gives  $\alpha$ -naphthylamine-2:5:7-trisulphonic acid.

(xiv)  $\alpha$ -Naphthylamine-5:8-disulphonic Acid is obtained from  $\alpha$ -nitronaphthalene-5:8-disulphonic acid by reduction in acid solution. The product, converted into sodium salt, gives in concentrated solution a precipitate of the acid sodium salt on acidification. Both the acid and the acid sodium salt,  $NaHA + 1\frac{1}{2}H_2O$ , form needles very sparingly soluble in water, but easily soluble in alkalis, giving greenish-yellow solutions (Bayer, G.P. 70857; Gattermann, Ber. 1899, 32, 1156).

**Reactions.**—It couples easily with diazotised bases. From its diazo-compound naphthalene-1:4:8-trisulphonic acid and naphthasultone-5-sulphonic acid can be obtained, and by the bisulphite method it yields the corresponding  $\alpha$ -naphthol-5:8-disulphonic acid. Digestion with 75% caustic potash solution at 150–160° converts it into 1-amino-8-naphthol-5-sulphonic acid, but with 60% solution at 250° into 1:8-dihydroxynaphthalene-4-sulphonic acid. With sodium amalgam,  $\alpha$ -naphthylamine is obtained (Gattermann, l.c.). By sulphonation with 40% anhydro-acid at 80–90° it forms naphthasultam-disulphonic acid-D.

(xv)  $\alpha$ -Naphthylamine-6:8-disulphonic Acid can be obtained from  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid by boiling with 75% sulphuric acid (Kalle, G.P. 83146); and is formed together with the 4:8-disulphonic acid

when acet- $\alpha$ -naphthalide-8-sulphonic acid is sulphonated with 25% anhydro-acid at the ordinary temperature, and the product boiled with water. The sodium salt is much more soluble than that of the 4:8-disulphonic acid, and, after removal of the latter by crystallisation from the concentrated solution, is separated as acid sodium salt from the filtrate by acidification. The salts in solution show green fluorescence; the acid sodium salt,  $\text{NaHA}$ , needles, is easily soluble (Bayer, G.P. 75084).

**Reactions.**—It couples easily with diazotised bases. From its very soluble diazo-compound, *naphthasultone-6-sulphonic acid*, and by elimination of the amino-group, *naphthalene-1:3-disulphonic acid* can be obtained. Digestion with 50% caustic potash solution at 180–200° converts it into 1-amino-8-naphthol-6-sulphonic acid.

#### $\alpha$ -NAPHTHYLAMINETRISULPHONIC ACIDS.

(i)  $\alpha$ -Naphthylamine-2:4:6-trisulphonic Acid is formed when  $\alpha$ -naphthylamine-6-sulphonic acid, or 4:6-disulphonic acid, is heated with 25% anhydro-acid (3·5 parts) at 50–60°, and afterwards with 70% anhydro-acid (1 part) at 80–90°. The acid sodium salt forms needles; it shows blue fluorescence in solution (Bayer, G.P.a. 7016; B.P. 15223, 1893).

**Reactions.**—It does not couple with diazotised bases (Bayer, l.c.). Heated with mineral acids it is converted into *a-naphthylamine-2:6-disulphonic acid* (Bayer, G.P.a. 31910), but with sodium amalgam in the cold it gives *a-naphthylamine-2:4-disulphonic acid*.

(ii)  $\alpha$ -Naphthylamine-2:4:7-trisulphonic Acid.—To obtain this acid,  $\alpha$ -naphthylamine-4-sulphonic acid is heated with 40% anhydro-acid at 120° (Höchst, G.P. 22545; B.P. 2178, 1882; cf. Armstrong and Wynne, Proc. C.S. 1890, 6, 125), or  $\alpha$ -naphthylamine-7-sulphonic acid (or 4:7-disulphonic acid) is heated with 25% anhydro-acid (3·5 parts) at 50–60°, and afterwards with 70% anhydro-acid (1 part) at 80–90° (Bayer, G.P.a. 6550; B.P. 15223, 1893; Frisch, Helv. Chim. Acta, 1930, 13, 768). It is also formed when 1:8-dinitronaphthalene is heated with sodium bisulphite solution and ammonia at 80–90°, and after removal of the less soluble sodium  $\alpha$ -naphthylamine-4:7-disulphonate (*q.v.*) by crystallisation, the 2:4:7-trisulphonate is separated from the mother-liquor by salting out (Höchst, G.P. 215338). The acid sodium salt forms small needles, shows blue fluorescence in alkaline solution, and does not couple with diazotised bases.

**Reactions.**—From its diazo-compound, *a-naphthol-2:4:7-trisulphonic acid*, and by elimination of the amino-group, *naphthalene-1:3:6-trisulphonic acid* are obtained. By digestion with water at 230° it yields *a-naphthylamine-2:7-disulphonic acid*, but when boiled with 75% sulphuric acid, the 7-monosulphonic acid.

(iii)  $\alpha$ -Naphthylamine-2:5:7-trisulphonic Acid is obtained when  $\alpha$ -naphthylamine-5-sulphonic acid is sulphonated with 35% anhydro-acid at 90–120° (Cassella, G.P. 188505), or when  $\alpha$ -naphthylamine-2:5- or -5:7-disulphonic acid is sulphonated with 40% anhydro-acid at 120–130° (Bayer, G.P.a. 7001; B.P. 17141b, 1893). Its acid disodium salt, isolated from the diluted

sulphonation product by salting out, forms needles easily soluble in water, and, like the acid, shows green fluorescence in solution.

**Reactions.**—Digestion with 50% caustic potash solution at 180–200° converts it into 1-amino-5-naphthol-2:7-disulphonic acid. When desulphonated either by sodium amalgam in the cold or by boiling with zinc dust and dilute caustic soda solution it yields *a-naphthylamine-2:7-disulphonic acid*.

(iv)  $\alpha$ -Naphthylamine-3:5:7-trisulphonic Acid is prepared by reduction of  $\alpha$ -nitronaphthalene-3:5:7-trisulphonic acid (Cassella, G.P. 75432). Its salts are easily soluble and in solution show green fluorescence.

**Reactions.**—From its diazo-compound *naphthalene-1:3:7-trisulphonic acid* and *a-naphthol-3:5:7-trisulphonic acid* can be obtained. Fusion with caustic soda at 160–170° converts it into 1-amino-5-naphthol-3:7-disulphonic acid. When desulphonated either by sodium amalgam in the cold or by boiling with zinc dust and dilute caustic soda solution it gives *a-naphthylamine-3:7-disulphonic acid*.

(v)  $\alpha$ -Naphthylamine-3:6:8-trisulphonic Acid, obtained by reduction of  $\alpha$ -nitronaphthalene-3:6:8-trisulphonic acid (Koch, G.P. 56058; B.P. 9258, 1890), is also formed when sodium  $\alpha$ -nitronaphthalene-3:8-disulphonate is warmed with sodium bisulphite solution (Fischer, G.P. 76438; B.P. 7046, 1894).

**Preparation.**—The product obtained by nitrating the trisulphonation melt consisting largely of naphthalene-1:3:6-trisulphonic acid, after dilution with water, is neutralised by lime, converted into sodium salt and the filtrate after acidification reduced hot by iron borings. After removal of the iron, the filtrate is concentrated, saturated with salt, and acidified, whereby a complete separation of the 3:6:8-trisulphonic acid as acid sodium salt is achieved, the mother-liquor containing nothing of any technical value (Heumann, "Anilinfarben," 1898, ii, 539).

**Identification.**—The acid disodium salt,  $\text{Na}_2\text{HA}$ , forms needles, and the normal sodium salt,  $\text{Na}_2\text{A} + 3\text{H}_2\text{O}$ , scales (Dressel and Kothe, Ber. 1894, 27, 2147). The solubilities of the acid and some of its salts in water at 18° are: the acid  $\text{H}_3\text{A} + 6\text{H}_2\text{O}$ , hair-like needles, 1:0·5 (1:8 in alcohol);  $\text{Na}_3\text{A} + 5\text{H}_2\text{O}$ , 1:3;  $\text{Na}_2\text{HA} + 4\text{H}_2\text{O}$ , 1:15 (sparingly soluble in brine and in dilute hydrochloric acid);  $\text{K}_3\text{A} + \text{H}_2\text{O}$ , 1:4;  $\text{Ca}_2\text{A}_2$ , 1:3. The di-aniline salt melts at 312° (Forster and Mosby, J.S.C.I. 1928, 47, 157r).

**Reactions.**—From its diazo-compound, *naphthalene-1:3:6-trisulphonic acid* (Dressel and Kothe, l.c.) and *naphthasultone-3:6-disulphonic acid* can be obtained. Digestion with water at 180–250° converts it into *a-naphthol-3:6:8-trisulphonic acid*, and with 30–40% caustic soda solution at 210° into 1-amino-8-naphthol-3:6-disulphonic acid (H acid).

Digestion with ammonia at 160–180° furnishes 1:3-diaminonaphthalene-6:8-disulphonic acid, and with aniline (or *p*-toluidine) at 150–160° diphenyl- (or di-*p*-tolyl)-1:3-diaminonaphthalene-6:8-disulphonic acid. By sulphonation with 25% anhydro-acid at 70–80° it yields *naphthasultam-3:4:6-trisulphonic acid*. When desulphonated



by boiling it with zinc dust and dilute caustic soda solution, *α*-naphthylamine-3:6-disulphonic acid is the product.

(vi) *α*-Naphthylamine-4:6:8-trisulphonic Acid is obtained by reduction of *α*-nitronaphthalene-4:6:8-trisulphonic acid (Bayer, G.P.a. 7006; G.P. 80741; B.P. 17141c, 1893; Kalle, G.P. 82563; B.P. 515, 1894).

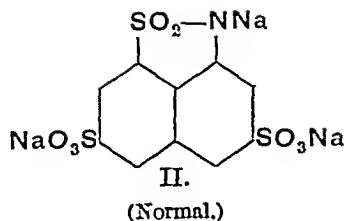
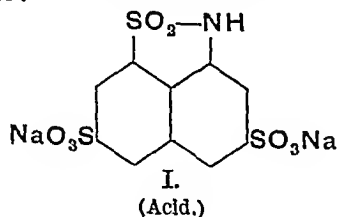
**Preparation.**—The nitration product obtained from the naphthalene-1:3:5-trisulphonic acid melt, after dilution with water, is neutralised by lime, and the filtrate, after acidification, reduced hot by iron borings, rendered alkaline by lime and converted into sodium salt. According to Swiss. P. 118720 the reduction is improved by presence of copper or nickel salts. From the concentrated solution, the acid sodium salt separates on the addition of hydrochloric acid.

**Reactions.**—It does not couple with diazotised bases. From its diazo-compound, *naphthalene-1:3:5-trisulphonic acid* (Kalle, l.c.) and *naphthasultone-4:6-disulphonic acid*, which is also formed by the bisulphite method, have been obtained. Boiled with 75% sulphuric acid it gives *α*-naphthylamine-6:8-disulphonic acid, and, digested with water at 160–220°, *α*-naphthol-6:8-disulphonic acid, the 4-sulphonic group being eliminated in both reactions, but when desulphonated by boiling with zinc dust and dilute caustic soda solution it is converted into *α*-naphthylamine-4:6-disulphonic acid. Fusion with caustic alkali gives 1-amino-8-naphthol-4:6-disulphonic acid (K-acid).

*α*-Naphthylamine-4:6:8-trisulphonic acid, condensed with 2-nitro-*p*-toluyl chloride, the product reduced, condensed with *m*-nitrobenzoyl chloride and, after reduction, converted into the carbamide by interaction with phosgene, provides the trypanocidal drug known as No. "309" or Bayer-205 (Fournau, Trefouel, Trefouel, and Vallée, Ann. Inst. Pasteur, 1924, 38, 81; cf. Compt. rend. 1924, 178, 675; Balaban and King, J.C.S. 1927, 3068).

#### NAPHTHASULTAM DERIVATIVES.

When warmed with anhydro-acid, *α*-naphthylaminesulphonic acids, in which one of the sulphonic groups occupies the *peri*-position relatively to the amino-radical, may undergo dehydration, forming naphthasultams, in addition to further sulphonation. Contrasted with the sultones the stability of the sultams is remarkable. Neither by boiling a sultam with caustic alkali solutions nor by heating it with ammonia is the anhydride ring attacked, although disruption of this ring (accompanied usually by partial desulphonation) can be effected if mineral acids be employed. These naphthasultamsulphonic acids, although not diazotisable, can be coupled with diazotised bases provided the 4-position be free. The salts are of two types:



Those of type I are colourless, but those of type II are yellow and give yellow solutions, which show intense green or yellowish-green fluorescence.

Not only naphthasultam, but its *N*-methyl ether, can couple with diazo-compounds, a fact which suggests that coupling is not necessarily due to the assumption of the enolic form (König and Köhler, Ber. 1922, 55 [B], 2139). In studying the analogy between naphthasultam and *α*-naphthol, König and Wagner have prepared a series of naphthasultam derivatives (*ibid.* 1924, 57 [B], 1056).

Naphthasultamsulphonic acids, containing a sulphonic group in position 3, are decomposed on heating with an aromatic amine and hydrochloric acid, the —NHR— group replacing the 3-sulphonic group (I.G., G.P. 442610).

(i) Naphthasultam has been obtained from *α*-naphthylamine-8-sulphonic acid by dehydration with phosphorus oxychloride. It melts at 177–178°, and in its behaviour towards chlorine presents many analogies with *α*-naphthol. On nitration, it yields 2:4-dinitronaphthasultam, pale yellow prisms soluble in caustic alkalis or alkali carbonates but almost insoluble in water (Dammert, J. Amer. Chem. Soc. 1907, 29, 1320; Bayer, G.P. 210222; cf. Zincke and Jülicher, Annalen, 1916, 411, 195; Zincke and Schurmann, *ibid.* 1918, 416, 75).

(ii) Naphthasultam-4-sulphonic Acid, obtained by the sulphonation of naphthasultam with monohydrate at 45°, crystallises in pale red needles easily soluble in water. Both the acid and its anilide are less reactive towards diazo-compounds than naphthasultam (König and Keil, Ber. 1922, 55 [B], 2149).

(iii) Naphthasultam-2:4-disulphonic Acid-S is obtained when *α*-naphthylamine-8-sulphonic acid or 4:8-disulphonic acid is sulphonated with 25–40% anhydro-acid at 80–90°, the operation being continued until a sample of the product diluted with water neither reacts with nitrito nor couples with diazotised bases (Bayer, G.P. 79566; B.P. 4979, 1893; Aktienges., G.P.a. 3346; B.P. 2984, 1893; Dressel and Kotho, Ber. 1894, 27, 2139). The corresponding *α*-naphthylamino-2:4:8-trisulphonic acid is unknown.

**Identification.**—The acid disodium salt,  $\text{Na}_2\text{HA} + 2\text{H}_2\text{O}$ , forms colourless needles, soluble in water without fluorescence, and the trisodium salt,  $\text{Na}_3\text{A} + 8\frac{1}{2}\text{H}_2\text{O}$ , yellow scales, easily soluble in water with green fluorescence.

**Reactions.**—Fusion with caustic soda at 170–180° converts it into 1-amino-8-naphthol-2:4-disulphonic acid. Digestion with 40% sulphuric acid at 110° furnishes *α*-naphthylamine-2:8-disulphonic acid, but with 20% hydrochloric acid at 140–160° *α*-naphthylamine-8-sulphonic acid. When heated in 50% sulphuric acid solution at

75–80° with nitric acid  $\rho$  1.2, it is converted successively into *nitronaphthasultamsulphonic acid* and 2:4-dinitronaphthasultam (Bayer, G.P. 210222).

(iv) Naphthasultam-3:6-disulphonic Acid is prepared by boiling the acid sodium salt of naphthasultam-3:(4):6-trisulphonic acid with 20% sulphuric acid. The *trisodium* salt,  $\text{Na}_3\text{A} + 4\text{H}_2\text{O}$ , forms easily soluble, small, yellow prisms (Bayer, G.P. 84139; Dressel and Kothe, Ber. 1894, 27, 2149).

*Reactions.*—Fusion with caustic soda at 180° converts it into 1-amino-8-naphthol-3:6-disulphonic acid. When boiled with 50% sulphuric acid, it gives  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid.

(v) Naphthasultamdisulphonic Acid- $\epsilon$  is obtained by heating sodium  $\alpha$ -naphthylamine-3:8-disulphonate with 40% anhydro-acid at 80–90° (Bayer, G.P. 79566; B.P. 4979, 1893).

(vi) Naphthasultamdisulphonic Acid-D, obtained by heating sodium  $\alpha$ -naphthylamine-5:8-disulphonate with 40% anhydro-acid at 80–90°, yields 1-amino-8-naphtholdisulphonic acid-D on fusion with caustic soda at 170° (Bayer, G.P. 79566; 80668; B.P. l.c.).

(vii) Naphthasultam-3:(4):6-trisulphonic Acid is formed when the acid sodium salt of  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid is heated with 25% anhydro-acid at 80° until a test no longer reacts with nitrite. The *acid sodium* salt,  $\text{Na}_3\text{HA} + 4\text{H}_2\text{O}$ , and the yellow *sodium* salt,  $\text{Na}_4\text{A} + 4\text{H}_2\text{O}$ , are easily, but the yellow *barium* salt is only sparingly soluble (Bayer, G.P. 84139; Dressel and Kothe, Ber. 1894, 27, 2147).

*Reactions.*—Digestion with 75% caustic potash solution at 130° converts it into 1-amino-8-naphthol-3:6-disulphonic acid. When boiled with 20% sulphuric acid it yields naphthasultam-3:6-disulphonic acid; and with 50% sulphuric acid  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid (Bayer, l.c.; Dressel and Kothe, l.c.).

(viii) Naphthasultam-(2):4:6-trisulphonic Acid is obtained when the acid sodium salt of  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid is heated with 25% anhydro-acid at 80–90° until a test no longer reacts with nitrite (Bayer, G.P. 84140). The *acid sodium* salt forms easily soluble needles; the *sodium* salt,  $\text{Na}_4\text{A} + 6\text{H}_2\text{O}$ , easily soluble, minute yellow prisms. When heated with caustic alkali at 150–160°, it is converted into 1-amino-8-naphthol-(2):4:6-trisulphonic acid (Bayer, G.P. 84597).

#### CHLORO- $\alpha$ -NAPHTHYLAMINES.

8-Chloro- $\alpha$ -naphthylamine can be obtained from 1:8-diaminonaphthalene by allowing its azimino derivative to interact with copper powder or with cuprous salts and hydrochloric acid at 30°. The base forms needles, m.p. 98° (Badische, G.P. 147852; cf. Atterberg, Ber. 1876, 9, 1730).

5:8-Dichloro- $\alpha$ -naphthylamine, obtained by reduction of 5:8-dichloro- $\alpha$ -nitro-naphthalene, forms needles, m.p. 104° (Widman, Bull. Soc. chim. 1877, [ii], 28, 510; Bayer, G.P. 293318).

8-Chloro- $\alpha$ -naphthylamine-5-sulphonic Acid is formed from the azimino derivative of 1:8-diaminonaphthalene-4-sulphonic acid by

interaction with copper powder (Badische, l.c.). When digested with 50% caustic soda solution at 190–195° it yields 1-amino-8-naphthol-5-sulphonic acid (Badische, G.P. 112778).

Several  $\alpha$ -chloro- $\alpha$ -naphthylaminesulphonic acids, prepared by nitrating  $\alpha$ -chloronaphthalenesulphonic acids and reducing the products, have been used in making azo-dyes, but not described in detail (Read, Holliday and Sons, B.P. 13999, 1897; 11736, 1898).

8-Chloro- $\alpha$ -naphthylamine-3:6-disulphonic Acid is prepared from the azimino derivative of 1:8-diaminonaphthalene-3:6-disulphonic acid by interaction with copper powder (Badische, G.P. 147852), or from  $\alpha$ -naphthylamine-3:6-disulphonic acid by conversion into the chloro-acid with subsequent nitration and reduction (Bayer, G.P. 289107). It crystallises from acid solution in needles.

*Reactions.*—It couples with diazotised bases. Fusion with caustic alkali converts it into 1-amino-8-naphthol-3:6-disulphonic acid, but when heated with dilute sulphuric acid under pressure it yields 8-chloro- $\alpha$ -naphthol-3:6-disulphonic acid.

Acylated by interaction with *m*-nitrobenzoyl chloride, followed by reduction and condensation with phosgene, it furnishes carbamide derivatives (Bayer, l.c.).

2:4-Dichloro- $\alpha$ -naphthylaminesulphonic Acid is formed when 2:4-dichloro-acet- $\alpha$ -naphthalide is sulphonated with 23% anhydro-acid below 45°, and the product deacetylated by boiling it with water. It is sparingly soluble in water; its *sodium* salt forms scales, and its *zinc* and *magnesium* salts long needles. When its sparingly soluble, crystalline diazo-compound is heated with sodium carbonate solution at 60°, it is converted into the *diazo-oxide* of 4-chloro-1-amino- $\beta$ -naphtholsulphonic acid (Badische, G.P. 153298; B.P. 16995, 1903).

#### NITRO- $\alpha$ -NAPHTHYLAMINES.

Direct nitration of  $\alpha$ -naphthylamine in concentrated sulphuric acid leads normally to the production of tarry impurities, but these can be avoided by working at –9° to –1° and stirring vigorously. The 5- and 8-nitro- $\alpha$ -naphthylamine sulphates thus formed can be separated by utilising the sparing solubility of the 5-derivative in *N*- to 3*N*-sulphuric acid. The free amines can be used as components in dyes (Morgan and Jones, J.S.C.I. 1923, 42, 341*r*). If the amino-group is acetylated before nitration, a mixture of the 2-nitro- and 4-nitro-isomers is obtained, which can be separated by passing dry hydrogen chloride into a nitrobenzene solution of the bases, when 4-nitro- $\alpha$ -naphthylamine hydrochloride is precipitated (Hodgson and Kilner, J.C.S. 1924, 807; Hodgson and Walker, *ibid.* 1933, 1205). On the other hand if the amino-group is protected by phthalic anhydride or substituted phthalic anhydrides, the compound is nitrated mostly in the 8-position (Hodgson and Crook, *ibid.* 1936, 1844). Protection of the amino-group by using its ethyl carbamide or carbamate derivative leads, on nitration followed by hydrolysis, to the formation of 2:4-dinitro- or 2:4:5-trinitro- $\alpha$ -naphthylamine (Groeneveld, Rec. trav. chim. 1931, 50, 681). 1:5- and 1:8-Nitronaphthyl-

amines can also be obtained by selective reduction of the dinitronaphthalenes (Ruggli and Knapp, *Helv. Chim. Acta*, 1930, 13, 763; Voroschov and Kulev, *B.* 1929, 934; I.C.I. and Hodgson, *B.P.* 392414).

From the 2- and 4-nitro- $\alpha$ -naphthylamines, derivatives of dinaphthylmethane have been obtained by condensation with formaldehyde (Morgan and Jones, *l.c.*, p. 92r). With methyl sulphate, the behaviour of nitro- $\alpha$ -naphthylamines varies, the 2-nitro- not being methylated, but the 8-nitro- giving the methyl derivative and the 3- and 5-nitro- the dimethyl derivative (Vesely and Vojtech, *A.* 1929, 437).

(i) 2-Nitro- $\alpha$ -naphthylamine is obtained as acetyl derivative, mixed with 4-nitroacet- $\alpha$ -naphthalide, by nitrating acet- $\alpha$ -naphthalide in acetic acid solution. By limited hydrolysis of the product with aqueous alcoholic caustic potash, 4-nitro- $\alpha$ -naphthylamine can be separated from the 2-nitroacet- $\alpha$ -naphthalide, which is most conveniently hydrolysed by boiling with alcoholic hydrochloric acid (Lellmann and Remy, *Ber.* 1886, 19, 797; Lellmann, *ibid.* 1887, 20, 892). It is also formed by aminating 1-chloro-2-nitronaphthalene in alcohol with ammonia at 180° (Hoogveen, *Rec. trav. chim.* 1931, 50, 37), and in 80% yield by the action of hydroxylamine in alcoholic alkaline solution on 2-nitronaphthalene (Meisenheimer and Patzig, *Ber.* 1906, 39, 2541).

*Identification.*—It crystallises from alcohol in reddish-yellow, monoclinic prisms, m.p. 144°, and its acetyl derivative in yellow needles, m.p. 199° (Lellmann, *ibid.* 1884, 17, 112). When boiled with excess of caustic potash solution it is converted into 2-nitro- $\alpha$ -naphthol.

2-Nitro-1-methylaminonaphthalene, m.p. 144°, and the ethylamino-compound, m.p. 77°, are prepared from 1-chloro-2-nitronaphthalene by Hoogveen's method (*l.c.*).

(ii) 3-Nitro- $\alpha$ -naphthylamine is produced when 1:3-dinitronaphthalene is reduced with hydrogen sulphide and alcoholic ammonia (Vesely and Dvorák, *Bull. Soc. chim.* 1923, [iv], 33, 319) or with sodium sulphide in methyl alcohol in presence of sodium bicarbonate (Hodgson and Birtwell, *J.C.S.* 1944, 75). At the same time 4-nitro- $\beta$ -naphthylamine is formed, the ratio being about 6 parts of the former to 1 part of the latter. The two amines can be separated by taking advantage of the more ready acetylation of 4-nitro-2-naphthylamine.

*Identification.*—3-Nitro- $\alpha$ -naphthylamine crystallises from 50% aqueous alcohol in orange yellow needles, m.p. 137°; formyl derivative, m.p. 216°, acetyl, 259°. Bromination gives 2:4-dibromo-3-nitro-1-naphthylamine, m.p. 182° (Hodgson and Hathaway, *J.C.S.* 1944, 21, 385).

(iii) 4-Nitro- $\alpha$ -naphthylamine, prepared from 4-nitroacet- $\alpha$ -naphthalide (*see supra*) by hydrolysis with alcoholic potash (Liebermann, *Annalen*, 1876, 183, 232), can also be obtained by mixing  $\alpha$ -naphthylloxamic acid with nitric acid ( $\rho$  1.36) at 30–40°, and hydrolysing the product with alkalis or mineral acids (Lange, *G.P.* 58227); or by heating  $\alpha$ -chloro-4-nitronaphthalene with 8% alcoholic ammonia at 150–170° (Griesheim, *G.P.* 117006; *B.P.* 7692, 1900);

or by oxidising 4-nitroso- $\alpha$ -naphthylamine with potassium permanganate.

*Identification.*—It crystallises from alcohol in orange needles, m.p. 196°, and its acetyl derivative in yellow needles, m.p. 190°. When boiled with aqueous caustic potash, it is converted into 4-nitro- $\alpha$ -naphthol.

4-Nitro- $\alpha$ -naphthylamine-5-sulphonic acid, obtained when  $\alpha$ -naphthylamine-5-sulphonic acid, dissolved in 20 times its weight of sulphuric acid, is nitrated below 10°, forms sparingly soluble, small needles, and its sodium salt yellow scales (Bayer, *G.P.* 133951; *B.P.* 9498, 1899; *cf.* Levinstein, *B.P.* 13178, 1899).

4-Nitro- $\alpha$ -naphthylamine-6-sulphonic and 7-sulphonic acids are obtained by the nitration of the corresponding  $\alpha$ -naphthylaminesulphonic acids or their acetyl derivatives in sulphuric acid solution. The 6-sulphonic acid and its salts, respectively, are less soluble than the 7-isomers (Cassella, *G.P.* 73502; 74177; *B.P.* 15444, 1893). Diazotised, these acids, singly or mixed, have been used as first component in azo-dyes.

(iv) 5-Nitro- $\alpha$ -naphthylamine can be prepared by partial reduction of 1:5-dinitronaphthalene with alcoholic hydrogen sulphide (Beilstein and Kuhlberg, *Annalen*, 1873, 169, 87); or by hydrolysis of 5-nitro- $\alpha$ -naphthylamine-4-sulphonic acid (Nietzki and Zübelen, *Ber.* 1889, 22, 452), or, mixed with the 4- and 8-compounds, by nitration of  $\alpha$ -naphthylamine dissolved in 10 times its weight of sulphuric acid (Meldola and Streatfeild, *J.C.S.* 1893, 63, 1055). The separation of the 4-, 5-, and 8-nitro-compounds can be effected by a method depending on the difference in solubilities of the salts (Hodgson and Crook, *J.C.S.* 1936, 1844).

*Identification.*—It crystallises in small, red needles, m.p. 119°, and its acetyl derivative in large, brown prisms, m.p. 220° (Badische, *G.P.* 145191). Its sulphate is less soluble than that of the 4- or 8-isomer.

5-Nitro- $\alpha$ -naphthylamine-2-sulphonic acid can be prepared by nitrating  $\alpha$ -naphthylamine-2-sulphonic acid in sulphuric acid solution below 15°. The acid and its diazo-compound are sparingly soluble (Cassella, *G.P.* 70890).

5-Nitro- $\alpha$ -naphthylamine-4-sulphonic acid is formed when acet- $\alpha$ -naphthalide-4-sulphonic acid, mixed with sulphuric acid, is nitrated in the cold, and the product deacetylated by boiling it with dilute acid. The acid, HA, crystallises in needles.

A nitro- $\alpha$ -naphthylaminesulphonic acid, probably isomeric with these acids, is obtained by reduction of 1:5-dinitronaphthalene-3-sulphonic acid with sodium sulphite or bisulphite (Höchst, *G.P.* 117268).

(v) 8-Nitro- $\alpha$ -naphthylamine is prepared by nitrating phthal- $\alpha$ -naphthylimide with nitric acid,  $\rho$  1.4, below 15°. The mixed nitro-compounds are hydrolysed with aqueous ammonia at 105°. The 5- and 4-isomers hydrolyse and are extracted with nitrobenzene. The remaining 8-nitro-compound is then hydrolysed similarly but at 120–130°. It crystallises from 90% formic acid (Hodgson and Crook, *J.C.S.* 1936, 1844) in red needles, m.p. 96–97°, picrate m.p. 139–141°, acetyl derivative m.p. 187–188°, benzoyl derivative m.p. 181°.

(vi) 2:3-Dinitro- $\alpha$ -naphthylamine is formed when 3-nitroacet- $\alpha$ -naphthalide is nitrated with nitric acid  $\rho$  1.50 below  $-3^\circ$ , and the resulting 2:3-dinitroacet- $\alpha$ -naphthalide, m.p.  $275^\circ$ , hydrolysed. It forms deep red needles from methyl alcohol-acetone, m.p.  $160$ – $161^\circ$  (Hodgson and Turner, J.C.S. 1943, 635).

(vii) 2:4-Dinitro- $\alpha$ -naphthylamine can be obtained from dinitroacet- $\alpha$ -naphthalide by hydrolysis with 50% sulphuric acid at  $100^\circ$  (Liebermann, Annalen, 1876, 183, 274; Meldola and Forster, Proc. C.S. 1893, 9, 8); or from 2:4-dinitro- $\alpha$ -naphthol by heating it with alcoholic ammonia under pressure at  $190$ – $200^\circ$  (Witt, Ber. 1886, 19, 2033; Morgan and Evens, J.C.S. 1919, 115, 1129). It crystallises in yellow needles, m.p.  $237^\circ$ , and its acetyl derivative in yellow needles, m.p.  $250^\circ$ .

**Reactions.**—When heated with aqueous alkalis, it is converted into 2:4-dinitro- $\alpha$ -naphthol. Diazotisation in concentrated sulphuric acid solution converts the base or its acetyl derivative into 4-nitronaphthalene-1-diazo-2-oxide (Friedländer, Ber. 1895, 28, 1951; Morgan and Evens, l.c.).

(viii) 4:5-Dinitro- $\alpha$ -naphthylamine is formed by the nitration of 5-nitroacet- $\alpha$ -naphthalide suspended in sulphuric acid, and hydrolysis of the product by boiling with dilute acid. It crystallises in orange scales, m.p.  $236^\circ$ , and its acetyl derivative in yellow needles, m.p.  $244^\circ$  (Badische, G.P. 145191; 158499).

#### $\beta$ -Naphthylamine.

The only practicable process for preparing  $\beta$ -naphthylamine is by the action of ammonia on  $\beta$ -naphthol, and this developed into a convenient manufacturing process after the discovery that, in presence of ammonium sulphite, the reaction took place at a lower temperature and more quickly than with ammonia alone. Some  $\beta\beta'$ -dinaphthylamine is formed as a by-product.

**Preparation.**— $\beta$ -Naphthol (114 parts) is heated with 22% ammonium sulphite solution (600 parts) and 20% ammonia (125 parts) at  $100$ – $105^\circ$  in an autoclave provided with a stirrer, until in the course of about 8 hours the conversion is complete. Above  $150^\circ$ ,  $\beta\beta'$ -dinaphthylamine begins to be formed. When cold, the  $\beta$ -naphthylamine is removed by filtration, the filtrate being used for a subsequent operation. It is then extracted by hot dilute caustic soda solution to remove  $\beta$ -naphthol, dissolved in dilute hydrochloric acid in which  $\beta\beta'$ -dinaphthylamine is insoluble, recovered from solution by the addition of alkali and finally distilled in a vacuum. The yield is almost quantitative (Badische, G.P. 117471; B.P. 1387, 1900; Bucherer, J. pr. Chem. 1904, [ii], 69, 88). The manufacturing process is based on this description, but less ammonium sulphite, more ammonia, and a higher temperature may be used.

Catalytically,  $\beta$ -naphthylamine is obtained in 90–95% yield by passing  $\beta$ -naphthol and ammonia over alumina at  $430$ – $450^\circ$  (Howald and Lowy, U.S.P. 1449423; Ind. Eng. Chem. 1923, 15, 397).

**Identification.**—It crystallises from alcohol in colourless, lustrous scales, melts at  $112^\circ$ , boils

at  $294^\circ$  (Liebermann and Jacobson, Annalen, 1882, 211, 41), is moderately volatile with steam, and dissolves easily in hot but only sparingly in cold water. The solutions of the base show blue fluorescence; those of its salts are non-fluorescent. The hydrochloride,  $B, HCl$ , forms non-fluorescent scales, easily soluble, and the nitrate,  $B, HNO_3$ , and sulphate,  $B_2, H_2SO_4$ , scales, sparingly soluble in water. The platinichloride crystallises in scales, and the picrate, from alcohol, in long yellow needles, m.p.  $195^\circ$ . Unlike  $\alpha$ -naphthylamine it gives no colour reactions with ferric chloride, chromic acid, bleaching powder, or nitrous acid.

**Reactions.**—It couples with diazotised bases as the end component of azo-dyes. From its diazo-compound,  $\beta$ -naphthol can be obtained (Liebermann, *ibid.* 1876, 183, 268). Its nitrate, by nitration, gives a mixture of 5-nitro- and 8-nitro- $\beta$ -naphthylamine. On sulphonation, it furnishes a series of mono-, di-, and tri-sulphonic acids. When heated alone, or with calcium or zinc chloride, it is converted partially into  $\beta\beta'$ -dinaphthylamine and ammonia, but with soda-mide, mixed with naphthalene at  $230^\circ$ , it gives 1:6-diaminonaphthalene. With excess of nitrous gases and subsequent warming below  $50^\circ$ ,  $\beta$ -naphthylamine hydrochloride suspended in water gives 1-nitro- $\beta$ -naphthol (Varma and Krishnamurthy, J. Indian Chem. Soc. 1926, 3, 326). It also forms red compounds, m.p.  $65$ – $3^\circ$  and  $61$ – $7^\circ$ , with 1-chloro- and 1-bromo-2:4-dinitrobenzene, respectively (Buehler, Hisey, and Wood, J. Amer. Chem. Soc. 1930, 52, 1939). Its reduction is described under tetralin derivatives.

**Analysis.**—Commercial  $\beta$ -naphthylamine is a distilled product, and is marketed as a coarse powder, not darker than pink-grey in colour. It should be at least 98.5% pure by titration with sodium nitrite solution, and should not begin to melt below  $109^\circ$ .

$\beta$ -Naphthylamine in the presence of  $\beta$ -naphthol,  $\beta\beta'$ -dinaphthylamine, and  $\alpha$ -naphthylamine can be determined by titration with sodium nitrite after the  $\beta$ -naphthol has been sulphonated (Lee and Jones, J. Ind. Eng. Chem. 1922, 14, 961).

#### Acyl Derivative.

Acetyl- $\beta$ -naphthylamine (acet- $\beta$ -naphthalide), is best prepared by boiling  $\beta$ -naphthylamine with 1.25–1.5 times its weight of glacial acetic acid for 12 hours, the  $\beta\beta'$ -dinaphthylamine (about 10%) formed being readily separated by crystallisation from alcohol, in which it is only sparingly soluble (Liebermann and Jacobson, Annalen, 1882, 211, 42).

**Properties.**—It crystallises in lustrous scales, m.p.  $132^\circ$  (Cosiner, Ber. 1881, 14, 59), dissolves readily in alcohol, but only sparingly in water, is more easily hydrolysed by dilute acids than by alkalis (Calm, *ibid.* 1882, 15, 610).

**Reactions.**—On chlorination, it yields 1-chloroacet- $\beta$ -naphthalide. It is converted by bleaching powder at  $0^\circ$  into the N-chloro-compound, but at  $20^\circ$  into 1-chloroacet- $\beta$ -naphthalide (Hoogveen, Rec. trav. chim. 1930, 49, 1093; 1931, 50, 37). Nitration converts it into 1-nitroacet- $\beta$ -naphthalide. By sulphonation with sul-

phuric acid, it furnishes *acet-β-naphthalide-5-sulphonic acid* at 20–30°, or *acet-β-naphthalide-7-sulphonic acid* at 150–160° (Kinzlberger, G.P.a. 5732), but with chlorosulphonic acid *acet-β-naphthalide-4-sulphonyl chloride*, m.p. 192° (Höchst, G.P. 292357).

#### Alkyl Derivatives.

Alkyl derivatives are conveniently prepared by interaction of the base with the appropriate ester of *p*-toluenesulphonic acid in the presence of alkali (Slotta and Franke, Ber. 1930, 63 [B], 678; Rodionov and Vedenski, A. 1932, 51).

**N-Methyl-β-naphthylamine**, obtained by heating β-naphthol (100 g.), methylamine hydrochloride (75 g.), and 5N-caustic soda solution (190 c.c.) under pressure at 200–220°, is an oil, b.p. 317°/766 mm. or 207°/60 mm., which yields a *nitrosamine*, needles, m.p. 88°, and an *acetyl* compound, prisms, m.p. 50–51° (Morgan and Evens, J.C.S. 1919, 115, 1141; cf. Pechmann and Heinze, Ber. 1897, 30, 1785; Pschorr and Karo, *ibid.* 1906, 39, 3142). The 6-*sulphonic acid* + H<sub>2</sub>O, m.p. 192°, is obtained by the interaction of methylamino hydrochloride with sodium 2-naphthol-6-sulphonate at 200° in presence of sodium hydroxide (Morgan and Rooke, J.S.C.I. 1922, 41, 1r).

**N-Dimethyl-β-naphthylamine**, prepared by heating β-naphthylamine (1 mol.) with methyl iodide (3 mol.), caustic soda (2.5 mol.), and water (5 mol.) at 120° for 5–6 hours, converting the quaternary iodide into chloride or hydroxide and evaporating the aqueous solution of either to dryness (Morgan, J.C.S. 1900, 77, 822; cf. Bamberger and Müller, Ber. 1889, 22, 1306), forms scales, m.p. 46°, b.p. 305°.

**N-Ethyl-β-naphthylamine**, obtained by boiling a solution of β-naphthylamine (10 parts) in alcohol (30 parts) with ethyl bromide (8.5 parts) during 12 hours (Fischer, Ber. 1893, 26, 193), is an oil, b.p. 305°/716 mm., 191°/25 mm. (Bamberger and Müller, *ibid.* 1889, 22, 1297), or 315–316°/760 mm. (Vaubel, Chem.-Ztg. 1903, 27, 278).

**Reactions.**—It couples with diazotised bases furnishing azo-dyes. On sulphonation with weak anhydro-acid at a moderate temperature, the 5-*sulphonic acid*, mixed with a small quantity of the 8-*sulphonic acid*, is formed; with monohydrate at 140° the 7-*sulphonic acid* is obtained; and with 20% anhydro-acid at 110–120°, the 5:7-*disulphonic acid* is produced.

**N-Diethyl-β-naphthylamine**, obtained by heating β-naphthylamine (39 g.), caustic soda (22 g.), water (22 c.c.), and ethyl iodide (85 g.) at 120° during 7–8 hours (Morgan, *l.c.*), is an oil, b.p. 316°/717 mm.

**N-Benzyl-β-naphthylamine** has m.p. 67.5°, b.p. 405° (Ciusa and Cremonini, Gazzotta, 1928, 58, 153).

#### Aryl Derivatives.

Phenyl-, tolyl-, and other aryl-β-naphthylamines can be prepared by heating β-naphthol with the respective base (or its hydrochloride) under pressure at 200–210° for 10 hours either alone (Graebe, Ber. 1880, 13, 1850; Badische, G.P. 14612; cf. Ochler, B.P. 2516 (prov. spec.), 1880), or with the addition of ammonia-zinc

chloride (Merz and Weith, Ber. 1880, 13, 1300). The yield is almost quantitative when β-naphthol (1 mol.), the base (2 mol.), and anhydrous calcium chloride (1 mol.), are heated together at 280° under pressure for 9 hours (Friedländer, *ibid.* 1883, 16, 2077), or when β-naphthol and the base are heated together with 1% of iodine at 180–190° during several hours (Knoll & Co., G.P. 241853; Knoovenagel and Sakow, J. pr. Chem. 1914, [ii], 89, 17), or with anilino hydrochloride at 230° for 4 hours (Tschernitzov and Drozhov, J. Appl. Chem. Russia, 1934, 7, 785). They can be obtained from β-naphthol or β-naphthylamine by interaction with an aromatic amine in the presence of sodium bisulphite (I.G., B.P. 282111). These products dissolve in the ordinary organic solvents, and, when heated with hydrochloric acid under pressure at 240°, regenerate β-naphthol and the base (Friedländer, *l.c.*). They are used for making dyes for acetate silk (I.G., *l.c.*), and phenyl-β-naphthylamine is an important constituent of rubber antioxidants.

**N-Phenyl-β-naphthylamine** is obtained when β-naphthol (144 parts), aniline (170 parts), and iodine (1–2 parts) are heated together at 180–190° during 7 hours, and the product, after successive extractions by dilute acid and by dilute caustic soda solution, is distilled in a vacuum (Knoll & Co., *l.c.*).

**Identification.**—It forms needles, m.p. 108°, b.p. 395° (Crafts, Annalen, 1880, 202, 5) or 237°/15 mm. (Knoll & Co., *l.c.*), is moderately soluble in cold solvents and in solution shows blue fluorescence. The *hydrochloride* is a crystalline powder, decomposed by water. The *acetyl* derivative, m.p. 93° (Streiff, *ibid.* 1881, 209, 157) has been used as a stabiliser for nitrocellulose powders (Ryan and Drumm, Proc. Roy. Irish Acad. 1918, 34 [B], (8), 165). The *nitroso* derivative forms prisms, m.p. 93° (Streiff, *l.c.*). The *toluene-p-sulphonyl* derivative, m.p. 133°, readily furnishes 1-*nitro*- and 1:6-*dinitro*-β-naphthylamine (Morgan and Micklethwait, J.C.S. 1912, 101, 148; Aktionges., G.P. 164130; B.P. 27497, 1904).

**Reactions.**—It couples with diazotised bases forming azo-dyes. When sulphonated with 4 times its weight of monohydrate below 50° it yields a mixture of the 5- and 8-*monosulphonic acids* (Zimmer, G.P. 45940; B.P. 13798, 1888; Clayton Anilino Co., G.P. 53649; B.P. 10934, 1889; Lesser, Ber. 1894, 27, 2364; Bayer, G.P. 70349; B.P. 7337A, 1892).

**N-o-Tolyl-β-naphthylamine**, prepared similarly to the phenyl derivative, forms scales, m.p. 95°, b.p. 235–237°/14 mm. (Knoll & Co., G.P. 241853). On sulphonation below 50° it gives a mixture of the 5- and 8-*monosulphonic acids* (Clayton Anilino Co., G.P. 57370; B.P. 5155, 1890; cf. Bayer, *l.c.*).

**N-p-Tolyl-β-naphthylamine**, forms scales, m.p. 103°, showing in solution blue fluorescence; its *acetyl* derivative, needles, m.p. 85° (Friedländer, Ber. 1883, 16, 2079).

**ββ'-Dinaphthylamine** is obtained in almost quantitative yield, by boiling a solution of β-naphthylamine (1 part) in alcohol (6 parts) with sodium bisulphite solution of 40° B<sub>é</sub> (6 parts) in a reflux apparatus for 24 hours (Bayer,

G.P. 114874; B.P. 22804, 1899), or by heating  $\beta$ -naphthylamine with 0.5% of iodine at 230° during 4 hours (Knoll & Co., G.P. 241853; Knoevenagel, J. pr. Chem. 1914, [ii], 89, 23).

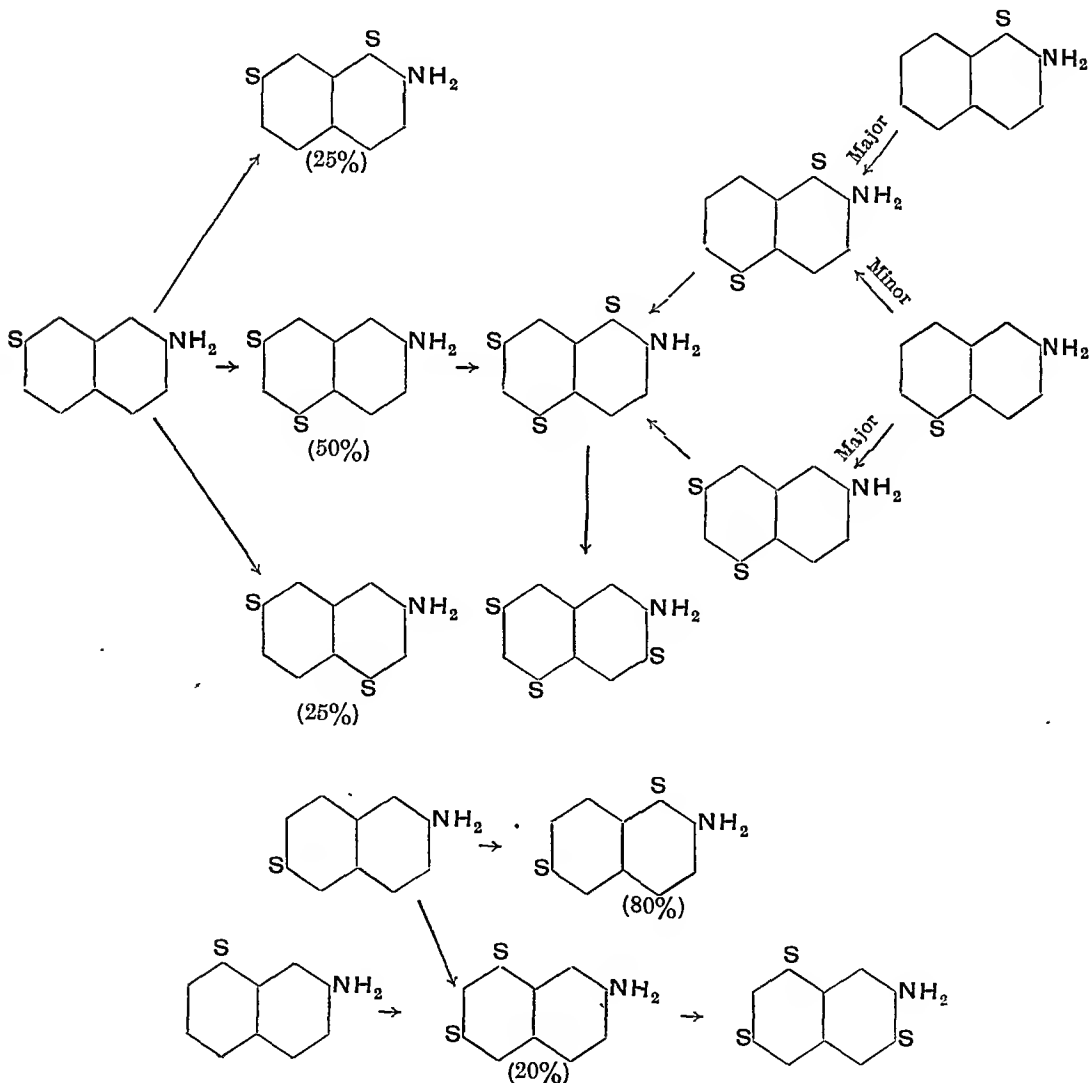
*Properties.*—It crystallises in scales, m.p. 171°, b.p. 471° (Ris, Ber. 1887, 20, 2619). Dissolved in alcohol or benzene, it shows intense blue fluorescence. When heated with hydrochloric acid at 240°, it yields  $\beta$ -naphthylamine and  $\beta$ -naphthol quantitatively (Ris, *ibid.* 1886, 19, 2017), and, with sulphuric acid, mixtures of the isomeric  $\beta$ -naphthylamine- and  $\beta$ -naphthol-sulphonic acids (Sandoz, G.P. 64859). Heated with sulphur it gives  $\beta$ -naphthathiazine (Fang, Sci. Rep. Tsing Hua Univ., 1937, 21).

#### Aryl- $\beta$ -naphthylaminesulphonic Acids.

Of the phenyl- (or *o*- or *p*-tolyl-)  $\beta$ -naphthylaminesulphonic acids, the 5-, 6-, 7-, or 8-sulphonic acid, and the 3:6- or 6:8-disulphonic acid can be obtained by heating the corresponding  $\beta$ -naphthylaminesulphonic acid with aniline (or *o*- or *p*-toluidine) and its hydrochloride at 160–170° (Bayer, G.P. 70349; 71158; 71168; B.P.

7337A, 1892). Less satisfactory results follow when the corresponding  $\beta$ -naphtholsulphonic acid is heated with the base and its hydrochloride at 190–200° (Aktienges., G.P. 38424), but if the bisulphite method is used good yields are obtained (Badische, G.P. 122570; B.P. 18726, 1900). The acids are moderately soluble in hot water; the sodium salts may be separated from solution by salting out. When coupled with diazotised bases they form azo-dyes which are bluer in shade than those from aryl- $\alpha$ -naphthylaminesulphonic acids.

$\beta\beta'$ -Dinaphthylamine-7:7'-disulphonic acid has been prepared from  $\beta$ -naphthylamine-7-sulphonic acid by the bisulphite method (Bayer, *l.c.*); the 5:5'-dihydroxy-7:7'-disulphonic acid from 2-amino-5-naphthol-7-sulphonic acid by the bisulphite method (Bayer, *l.c.*) or by heating it with water under pressure at 200°; and the 8:8'-dihydroxy-6:6'-disulphonic acid by the latter method (Bayer, G.P. 121094; B.P. 24296, 1899). The dihydroxy-compounds couple with diazotised bases, yielding azo-dyes (*cf.* Bayer, G.P. 114841; 221124; B.P. 24296, 1899).





**$\beta$ -NAPHTHYLAMINESULPHONIC ACIDS.**

$\beta$ -Naphthylaminesulphonic acids are obtained by the following methods:

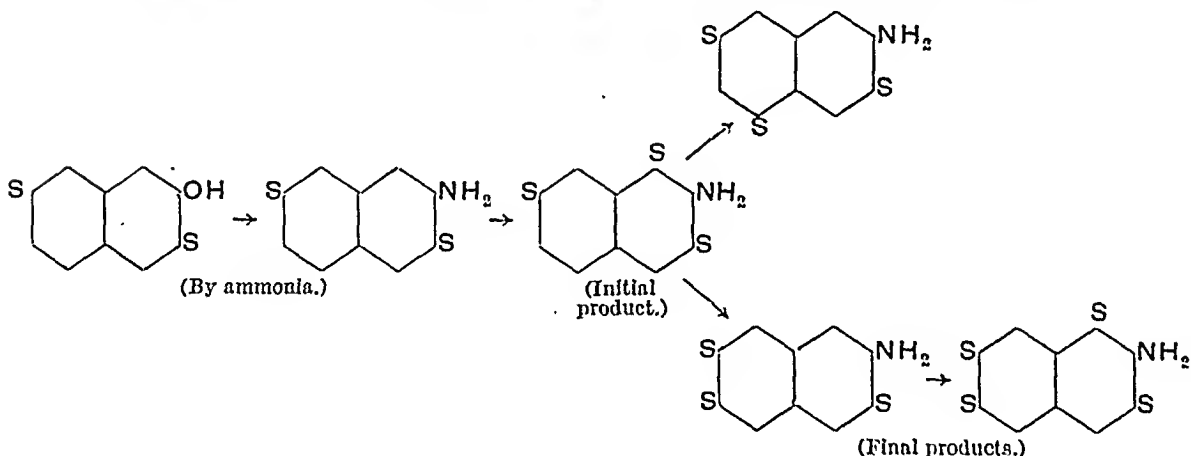
1. By sulphonation of  $\beta$ -naphthylamine or of the derived  $\beta$ -naphthylaminesulphonic acids. The product in most cases is a mixture of acids, from which the more soluble constituents cannot easily be obtained pure.  $\beta$ -Naphthylamine-1-sulphonic acid is obtained by sulphonation with chlorosulphonic acid in an organic solvent, other isomers being also formed.
2. By heating the sodium salts of the corresponding  $\beta$ -naphtholsulphonic acids with ammonia under pressure, preferably with ammonium sulphite present which enables a much lower temperature to be used. The process is applicable to all acids which do not contain a 4-sulphonic group, and is of value for the production of the 1-, 6-, 7-, or 8-monosulphonic acid, as each of the corresponding  $\beta$ -naphtholsulphonic acids is obtained in a pure state much more easily from  $\beta$ -naphthol than is the  $\beta$ -naphthylaminesulphonic acid from the mixed acids of the sulphonation melt (cf. Bucherer, J. pr. Chem. 1904, [ii], 70, 357).
3. By reduction of  $\beta$ -nitronaphthalenesulphonic acids. Only two acids are obtained in this way, viz. the 4:7- and

the 4:8-disulphonic acids, but for the production of the latter no other mode of preparation has been described.

Four monosulphonic acids, all of them heteronuclear, are known to be formed by the sulphonation of  $\beta$ -naphthylamine with sulphuric acid; six disulphonic acids by the sulphonation of monosulphonic acids; and six trisulphonic acids by the sulphonation of disulphonic acids. For the sulphonation of  $\beta$ -naphthylamine, sulphuric acid may be used, but for that of the monosulphonic acids, anhydro-acid is required. The effects of concentration of the acid, of temperature, and of duration of the reaction on the nature of the product, correspond with those traced out in other cases of sulphonation. It should be noted that sulphonation in the 1-position with sulphuric acid and oleum occurs only when at least one other sulphonic group is present in the molecule, and that the 1-sulphonic group when present is the first to be eliminated by hydrolysis.

The schemes given opposite illustrate the order in which sulphonic groups are introduced into the molecule of the isomeric monosulphonic acids.

The transformation into the 3:5:7-trisulphonic acid which  $\beta$ -naphthylamine-1:5:7-trisulphonic acid undergoes in the presence of 40% anhydro-acid at 140° is only less remarkable than that which has been shown to occur with the 1:3:7-trisulphonic acid under similar conditions:



$\beta$ -Naphthylaminemonosulphonic acids are very sparingly soluble in water. The di- and trisulphonic acids dissolve easily in water, but their acid salts are less soluble, and are precipitated instead of the acids when a mineral acid is added to solutions of their alkali salts.

As sources of azo-dyes, the  $\beta$ -naphthylaminesulphonic acids are less important than the  $\alpha$ -compounds. Many of the dyes obtained by coupling them with tetrazo derivatives are of little value (cf. Cassella, G.P. 46711); moreover, the  $\beta$ -sulphonic acids cannot be used as middle components in polyazo-dyes, as the amino-radical, after coupling has taken place in the *ortho*-position relatively to it, does not interact with nitrite to form a diazo-compound, but an azimino-like derivative which is incapable of coupling (cf. Bayer, G.P. 79816; B.P. 9972, 1893).

$\beta$ -Naphthylaminesulphonic acids containing either 1- or 8-sulphonic groups do not form azo-dyes, but yield diazo-amino-compounds when coupled with diazotised bases. Those containing a 1-sulphonic group exchange it for hydroxyl, giving the diazo-oxides of 2-amino-1-naphthol derivatives when diazotised and afterwards warmed at 50–60° with excess (2 mol.) of sodium carbonate solution (cf. Badische, G.P. 148882).

$\beta$ -Naphthylaminesulphonic acids containing a 4-sulphonic group, like the *m*-sulphonic acids from  $\alpha$ -naphthylamine, yield hydroxytoluic acids by prolonged heating with caustic alkali solution at 280°, but, unlike them, are not converted into diamionaphthalenes when heated under pressure with ammonia.

Unlike  $\alpha$ -naphthylaminesulphonic acids which, when digested with caustic alkali solution, exchange the amino- for a hydroxyl radical,  $\beta$ -



naphthylaminesulphonic acids, under similar conditions, retain the amino-group, exchanging an  $\alpha$ -sulphonic for a hydroxyl radical, thus furnishing aminonaphtholsulphonic acids of which they are an important source.

From  $\beta$ -naphthylamine-3:6- and 5:7-disulphonic acids, carbamide derivatives have been obtained by methods similar to those employed with  $\alpha$ -naphthylaminesulphonic acids (Bayer, G.P. 288273).

#### $\beta$ -NAPHTHYLAMINEMONOSULPHONIC ACIDS.

(i)  $\beta$ -Naphthylamine-1-sulphonic Acid (*Tobias acid*) is manufactured by heating  $\beta$ -naphthol-1-sulphonate with ammonia and ammonium sulphite (Bucherer, J. pr. Chem. 1904, [ii], 70, 357; Badische, G.P. 117471; B.P. 1387, 1900). It is also obtained by sulphonating  $\beta$ -naphthylamine with chlorosulphonic acid (B.D.C., B.P. 175019, 1920) or with sulphur trioxide (Du Pont, U.S.P. 1969189) in an inert solvent.

*Identification.*—The acid separates in sparingly soluble anhydrous scales from hot, or in efflorescent hydrated needles from cold water; the sodium salt,  $\text{NaA} + \text{H}_2\text{O}$ , in easily soluble scales, which give a non-fluorescent solution (*Tobias*, G.P. 74688). It is convertible into  $\beta$ -chloronaphthalene-1-sulphonyl chloride, m.p.  $76^\circ$ , and 1:2-dichloronaphthalene (Armstrong and Wynne, Proc. C.S., 1895, 11, 238; Tobias, B.P. 15404, 1893).

*Reactions.*—Diazotised, it forms the first component in certain important azo-dyes (cf. Badische, G.P. 112833; B.P. 25511, 1899). From its sparingly soluble, crystalline diazo-compound,  $\beta$ -naphthol-1-sulphonic acid has been obtained (*Tobias*, l.c.). When heated at  $230^\circ$  in a dry neutral atmosphere, its sodium salt is converted into sodium  $\beta$ -naphthylsulphamate (*Tobias*, l.c.). On sulphonation with 20% anhydro-acid it yields  $\beta$ -naphthylamine-1:5-disulphonic acid.

(ii)  $\beta$ -Naphthylamine-4-sulphonic Acid is obtained when  $\beta$ -naphthol-4-sulphonic acid is heated with ammonia under pressure (Kalle, G.P. 78603), or, mixed with the 8-sulphonic acid, when  $\beta$ -naphthylamine-4:8-disulphonic acid is boiled with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934).

*Identification.*—The acid,  $\text{HA} + \text{H}_2\text{O}$ , crystallises in sparingly soluble, long, white needles; the potassium salt,  $\text{KA} + 1\frac{1}{2}\text{H}_2\text{O}$ , in small needles; and the sodium salt,  $\text{NaA} + 4\text{H}_2\text{O}$ , in scales. The solution of the sodium salt shows violet fluorescence.

*Reactions.*—It couples with diazotised bases forming azo-dyes. Its diazo-compound is only sparingly soluble. Digestion with 60% caustic soda solution at  $230$ – $280^\circ$  converts it into o-toluic acid (Kalle, G.P. 79028; B.P. 16559, 1894).

(iii)  $\beta$ -Naphthylamine-5-sulphonic Acid originally prepared by Dahl (*Dahl's  $\gamma$ -acid*) is the main product, the minor product being the 8-sulphonic acid, of sulphonating  $\beta$ -naphthylamine with sulphuric acid (or oleum) at low temperature, the proportion formed varying with the temperature and amount of acid (Dahl, G.P. 32276, Green and Vakil, J.C.S. 1918, 113,

38) or acet- $\beta$ -naphthalide can be similarly sulphonated and deacetylated (Kinzlberger, G.P.a. 5732). It is most conveniently prepared from 2-naphthylamine-1:5-disulphonic acid (easily obtained from Tobias acid) by heating with dilute sulphuric acid to remove the 1-sulphonic acid group.

*Identification.*—The acid, HA, forms needles or scales, soluble in 260 parts of boiling or 3,000 parts of cold water. The salts dissolve easily in water, and, like the acid, show reddish-blue fluorescence in dilute solution. The barium salt,  $\text{BaA}_2 + 2\frac{1}{2}\text{H}_2\text{O}$ , forms granular aggregates; the calcium salt,  $\text{CaA}_2 + 11\text{H}_2\text{O}$ , needles, soluble in 11 parts of cold water; the potassium salt,  $\text{KA} + \text{H}_2\text{O}$ , small rhombohedra; the sodium salt,  $\text{NaA} + 5\text{H}_2\text{O}$ , prisms, soluble in 10 parts of boiling 95% alcohol; the ammonium salt, plates (cf. Forsling, Ber. 1887, 20, 2103). It is convertible into  $\beta$ -chloronaphthalene-5-sulphonyl chloride, prisms, m.p.  $70^\circ$ , and 1:6-dichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1889, 5, 48; Cleve, Ber. 1892, 25, 2481; Forsling, l.c.).

*Reactions.*—From its sparingly soluble diazo-compound,  $\beta$ -naphthol-5-sulphonic acid has been obtained. Fusion with caustic potash at  $260$ – $270^\circ$  converts it into 2-amino-5-naphthol. On sulphonation with 20% anhydro-acid in the cold it yields a mixture of  $\beta$ -naphthylamine-5:7-disulphonic acid with the 1:5-disulphonic acid as minor product.

(iv)  $\beta$ -Naphthylamine-6-sulphonic Acid ( $[\beta]$ -acid; *Brömer acid*) occurs to the extent of about 50% in the product formed when  $\beta$ -naphthylamine sulphate, or  $\beta$ -naphthylamine-5- or 8-sulphonic acid is heated with three times its weight of sulphuric acid at  $160$ – $170^\circ$  for 2 hours (see the 7-sulphonic acid). It is also produced, mixed with a small proportion of the 7-sulphonic acid (Bayer and Duisberg, Ber. 1887, 20, 1429), when  $\beta$ -naphthylamine hydrogen sulphate is baked at  $200$ – $210^\circ$  for 2 hours (Liebmann, G.P.a. 3205); or when  $\beta$ -naphthylamine is heated with three times its weight of potassium bisulphate at about  $230^\circ$  (Bischoff and Brodsky, Ber. 1890, 23, 1914).

*Preparation.*— $\beta$ -Naphthylamine-6-sulphonic acid and its salts, being much less soluble in water than the 7-compounds, can be separated without much difficulty by fractional crystallisation from the products obtained either by sulphonating  $\beta$ -naphthylamine under the conditions just described, or by heating impure  $\beta$ -naphthol-6-sulphonic acid, containing the 7-isomer, with ammonia (cf. Green, J.C.S. 1889, 55, 37; B.P. 15849, 1888).

The pure acid is obtained when  $\beta$ -naphthol-6-sulphonic acid is heated with aqueous ammonia in presence of ammonium sulphite (Bucherer, J. pr. Chem. 1904, [ii], 70, 357, Badische, G.P. 115335; 117471; B.P. 1387, 1900).

*Identification.*—The acid,  $\text{HA} + \text{H}_2\text{O}$ , crystallises in scales, soluble in 630 parts of boiling water (Weinberg, Ber. 1887, 20, 2909) or in 7,000 parts cold water (Waterman and Groot, Chem. Weekblad, 1928, 25, 40), and, like its salts, shows blue fluorescence in solution. The lead salt,  $\text{PbA}_2 + 2\text{H}_2\text{O}$ , forms scales, soluble in 670 parts of water at  $1^\circ$ ; the barium salt,

$\text{BaA}_2 + 6\text{H}_2\text{O}$ , long needles, soluble in 450 parts of cold water; the *calcium* salt,  $\text{CaA}_2 + 6\text{H}_2\text{O}$ , scales, soluble in 225 parts of water at  $5^\circ$ ; the *potassium* salt,  $\text{KA} + \text{H}_2\text{O}$ , silky needles, soluble in 40–50 parts of cold water; the *sodium* salt,  $\text{NaA} + 2\text{H}_2\text{O}$ , silky needles, soluble in about 40 parts of cold water, and easily in hot 90% alcohol (cf. Forsling, Ber. 1887, 20, 77; Limpricht, quoted by Schultz, "Chemie des Steinkohlenth," 3rd ed., i, 209). The *ammonium* salt,  $\text{NH}_4\text{A} + \text{H}_2\text{O}$ , large thin plates, is the least soluble of the ammonium  $\beta$ -naphthylaminesulphonates in cold water (Green, l.c.). It is convertible into  $\beta$ -chloronaphthalene-6-sulphenyl chloride, prisms, m.p.  $109^\circ$ , and 2:6-dichloronaphthalene (Forsling, l.c.; cf. Armstrong and Wynne, Proc. C.S. 1889, 5, 52).

**Reactions.**—It couples with diazotised bases forming the end component of some disazo-dyes. From its moderately soluble yellow diazo-compound or by the bisulphite method,  $\beta$ -naphthol-6-sulphonic acid can be obtained. On sulphonation with 20% anhydro-acid at  $20^\circ$ , it yields a mixture of  $\beta$ -naphthylamine:1:6-disulphonic acid with about 20% of the 6:8-disulphonic acid.

Substitution derivatives in which methyl, phenyl, and fuchsin radicles respectively occur in the amino-group of  $\beta$ -naphthylamine-6-sulphonic acid can be obtained by the Bucherer method if methylamine, aniline, and fuchsin are used in place of ammonia (Badische, G.P. 121683; 122570; 125589; B.P. 18726, 1900).

(v)  $\beta$ -Naphthylamine-7-sulphonic Acid ( $[\delta^-]$  acid; *F-acid*) is obtained, mixed with about an equal quantity of the 6-sulphonic acid (Schultz, Ber. 1887, 20, 3159), when  $\beta$ -naphthylamine is heated with sulphuric acid at temperatures above  $150^\circ$  (Bayer, G.P. 39925; 41505; B.P. 5846, 1886). It is also said to be the product when acet- $\beta$ -naphthalide is heated with 6 times its weight of sulphuric acid at  $150$ – $160^\circ$  for 1–1½ hours, and the product deacetylated by pouring the hot melt into water (Kinzlberger, G.P.a. 5732). The pure acid is obtained when sodium  $\beta$ -naphthol-7-sulphonate is heated with ammonia and ammonium sulphite (Bucherer, J. pr. Chem. 1904, [ii], 70, 357; Badische, G.P. 117471; B.P. 1387, 1900).

**Identification.**—The acid,  $\text{HA} + \text{H}_2\text{O}$ , forms slender, voluminous needles soluble in 350 parts of boiling water or 5,000 parts cold water (Waterman and Groot, l.c.). When boiled with a quantity of water insufficient to dissolve it, the crystalline acid changes into a very sparingly soluble, anhydrous, sandy powder. The *barium* salt,  $\text{BaA}_2 + 5\text{H}_2\text{O}$ , forms thin scales, soluble in 400 parts of cold water; the *calcium* salt,  $\text{CaA}_2 + 6\text{H}_2\text{O}$ , scales, soluble in 270 parts of cold water; the *potassium* salt, needles, soluble in 40 parts of cold water; the *ammonium* salt, small plates; the *sodium* salt,  $\text{NaA} + 4\text{H}_2\text{O}$ , small needles, soluble in hot 90% alcohol and in 70 parts of cold water. The solutions of the salts show reddish-violet fluorescence. It is convertible into  $\beta$ -chloronaphthalene-7-sulphonyl chloride, prisms, m.p.  $86^\circ$  (Armstrong and Wynne, Proc. C.S. 1889, 5, 49; Cleve, Ber. 1892, 25, 2484), and 2:7-dichloronaphthalene

(Erdmann, *ibid.* 1888, 21, 638; Armstrong and Wynne, l.c.).

**Reactions.**—It couples with diazotised bases, being the end component of some disazo-dyes. From its orange-red diazo-compound, or by the bisulphite method,  $\beta$ -naphthol-7-sulphonic acid can be obtained. Digestion with 50% caustic soda solution at  $260$ – $280^\circ$  converts it into 2-amino-7-naphthol. Heated with 20% sodium bisulphite solution at  $90$ – $100^\circ$  for 24 hours, its sodium salt is converted into sodium  $\beta\beta'$ -dinaphthylamine-7:7'-disulphonate. On sulphonation with 20–25% anhydro-acid at the ordinary temperature, it yields three  $\beta$ -naphthylaminedisulphonic acids, viz. the 1:7-, 4:7-, and 5:7-isomers.

The dimethyl derivative, obtained by heating the acid with dimethylamine under pressure at  $220^\circ$ , is converted into 2-dimethylamine-7-naphthol by fusion with caustic alkali (Geigy, G.P. 90310).

(vi)  $\beta$ -Naphthylamine-8-sulphonic Acid ( $[\alpha^-]$  acid; *Badische acid*) is formed (39–44%), together with the 5-sulphonic acid and about 1% of the mixed 6- and 7-isomers, when  $\beta$ -naphthylamine is heated with three times its weight of sulphuric acid at  $100$ – $105^\circ$  for about 6 hours (Badische, G.P. 20760; Dahl, G.P. 29084; B.P. 7712, 1884; Green and Vakil, J.C.S. 1918, 113, 38; Green, *ibid.* 1889, 55, 36). The proportion of the 8-sulphonic acid does not exceed 45% when  $\beta$ -naphthylamine sulphate is sulphonated with three times its weight of sulphuric acid at  $15$ – $20^\circ$ , while it amounts only to 30% when  $\beta$ -naphthylamine is sulphonated with three times its weight of 20% anhydro-acid at  $70$ – $80^\circ$  (Dahl, l.c.; Green, l.c.). The acid is also obtained when  $\beta$ -naphthol-8-sulphonic acid is heated with ammonia under pressure (Bayer, G.P. 42273; Pfützinger and Duisberg, Ber. 1889, 22, 397), or when the bisulphite reaction is applied to it (Bucherer, J. pr. Chem. 1904, [ii], 70, 358; Badische, G.P. 117471; B.P. 1387, 1900).

**Preparation.**—The product obtained by sulphonating  $\beta$ -naphthylamine sulphate with three times its weight of sulphuric acid at  $15$ – $20^\circ$  is converted into sodium salt, which, as a dry powder, is extracted with 90–95% alcohol to remove the isomeric salts, the residue consisting of the pure sodium  $\beta$ -naphthylamine-8-sulphonate (Dahl, l.c.; Green, l.c.; see the 5-sulphonic acid). An alternative method of separation is preferential precipitation from sodium salt solutions, the 2:8-acid precipitating first (Levi, Giorn. Chim. Ind. 1921, 3, 97).

**Identification.**—The acid forms slender needles, soluble in 200 parts of boiling or in 1,700 parts of cold water. The salts, like the acid, show blue fluorescence in dilute solution (cf. Forsling, Ber. 1887, 20, 2100). The *barium* salt,  $\text{BaA}_2 + 4\text{H}_2\text{O}$ , forms prisms, soluble in 23 parts of cold water; the *calcium* salt,  $\text{CaA}_2 + 6\text{H}_2\text{O}$ , prisms, soluble in 11 parts of cold water; the *potassium* salt,  $\text{KA} + \frac{1}{2}\text{H}_2\text{O}$ , six-sided prisms; the *sodium* salt,  $\text{NaA}$  (Erdmann, Annalen, 1893, 275, 281), large prisms, insoluble in alcohol; the *ammonium* salt (Green, l.c.), large solid prisms. It is convertible into  $\beta$ -chloronaphthalene-8-sulphonyl chloride, needles, m.p.  $129^\circ$ , and 1:7-dichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1888,

4, 105; 1889, 5, 53; Forsling, *l.c.*; Ber. 1888, 21, 2803; 1889, 22, 619).

**Reactions.**—It does not furnish azo-dyes by coupling with diazotised bases, but soluble yellow diazoamino-compounds (Witt, *ibid.* 1888, 21, 3483; Erdmann, *l.c.*). From its sparingly soluble diazo-compound or by the bisulphite method *β*-naphthol-8-sulphonic acid can be obtained. Fusion with caustic alkali at 260–270° converts it into 2-amino-8-naphthol. On sulphonation in the cold with 20% anhydro-acid, it gives *β*-naphthylamine-6:8-disulphonic acid.

#### *β*-NAPHTHYLAMINEDISULPHONIC ACIDS.

(i) *β*-Naphthylamine-1:5-disulphonic Acid is obtained when *β*-naphthylamine-1-sulphonic acid is sulphonated with 20% anhydro-acid in the cold (Armstrong and Wynne, Proc. C.S. 1895, 11, 238); or (as minor product) mixed with the 5:7-disulphonic acid when *β*-naphthylamine-5-sulphonic acid is sulphonated under similar conditions (Armstrong and Wynne, *ibid.* 1890, 6, 129).

**Identification.**—The normal potassium salt is moderately soluble in water, and convertible into *β*-chloronaphthalene-1:5-disulphonyl chloride, prisms, m.p. 158°, and 1:2:5-trichloronaphthalene (Armstrong and Wynne, *l.c.*).

**Reactions.**—From its sparingly soluble diazo-compound, the diazo-oxide of 2-amino-1-naphthol-5-sulphonic acid is obtained either by addition of sodium carbonate at 50–60° to remove free mineral acid, or by oxidation with sodium hypochlorite in alkaline solution (Badische, G.P. 145906; B.P. 6615, 1902; G.P. 160536; B.P. 4997, 1904). Fusion with caustic alkali at 210–230° converts it into 2-amino-5-naphthol-1-sulphonic acid. *β*-Naphthylamine-1:5-disulphonic acid, when heated with 75% sulphuric acid, is hydrolysed to give a mixture of *β*-naphthylamine and its 5-sulphonic acid. With stronger acid at 100°, *β*-naphthylamine-5-sulphonic acid only is produced, above 100°, the 6-sulphonic acid and, above 130°, the 6- mixed with the 7-sulphonic acids (Bucherer and Wahl, J. pr. Chem. 1921, [ii], 103, 129). On sulphonation with 40% anhydro-acid at 100°, it yields *β*-naphthylamine-1:5:7-trisulphonic acid.

(ii) *β*-Naphthylamine-1:6-disulphonic Acid is obtained as chief product, with about 20% of the 6:8-disulphonic acid, when *β*-naphthylamine-6-sulphonic acid is sulphonated with 20% anhydro-acid at a temperature below 20° (Armstrong and Wynne Proc. C.S. 1890, 6, 130; cf. Forsling, Ber. 1888, 21, 3495); or, pure, by applying the bisulphite reaction to sodium *β*-naphthol-1:6-disulphonate (Badische, G.P. 117471; B.P. 1387, 1900).

**Identification.**—The normal potassium salt,  $K_2A + 2H_2O$ , large crystals, the sodium salt, long needles, and the ammonium salt,  $(NH_4)_2A + H_2O$ , triclinic forms, are very soluble; but the acid potassium salt,  $KHA + H_2O$ , and acid sodium salt,  $NaHA + 2H_2O$ , long needles, are only sparingly so, and in dilute solution show blue fluorescence (Forsling, *l.c.*). It is convertible into *β*-chloronaphthalene-1:6-disulphonyl chloride, prisms, m.p. 124.5°, and 1:2:6-trichloronaphthalene (Forsling, *l.c.*; Armstrong and Wynne, *l.c.*).

**Reaction.**—Its sparingly soluble, crystalline diazo-compound, when warmed with excess of sodium carbonate solution, yields the diazo-oxide of 2-amino-1-naphthol-6-sulphonic acid (Badische, G.P. 148882; B.P. 6615, 1902).

(iii) *β*-Naphthylamine-1:7-disulphonic Acid, formed (29%), together with the 4:7- and 5:7-disulphonic acids, when *β*-naphthylamine-7-sulphonic acid is sulphonated in the cold with 20–25% anhydro-acid, is separated from the product by converting it into normal potassium salt, and collecting the least soluble portion by fractional crystallisation (Bayer, G.P. 79243; Dressel and Kothe, Ber. 1894, 27, 1194). It is also obtained when potassium *β*-naphthol-1:7-disulphonate is heated with ammonia and ammonium sulphite (Badische, G.P. 117471; B.P. 1387, 1900).

**Identification.**—The normal barium salt, moderately soluble needles, the potassium salt,  $K_2A + 3H_2O$ , large monosymmetric crystals; and the acid potassium salt, sparingly soluble slender needles, give solutions showing violet-blue fluorescence (Dressel and Kothe, *l.c.*).

**Reactions.**—In acetic acid solution it does not couple with diazobenzene (Bayer, G.P.a. 7274). From its easily soluble diazo-compound, *β*-naphthol-1:7-disulphonic acid can be obtained, and, when warmed with sodium carbonate solution, the diazo-oxide of 2-amino-1-naphthol-7-sulphonic acid (Badische, G.P. 148882; B.P. 6615, 1902). Prolonged boiling with 20% hydrochloric acid converts it into *β*-naphthylamine-7-sulphonic acid (Dressel and Kothe, *l.c.*).

(iv) *β*-Naphthylamine-3:6-disulphonic Acid (*β*-naphthylamine-[a]-disulphonic acid; amino-R-acid) is obtained from sodium *β*-naphthol-3:6-disulphonate by heating under pressure with ammonia and ammonium sulphite (Badische, G.P. 117471; B.P. 1387, 1900). It is also formed when sodium *β*-naphthylamine-3:6:8-trisulphonate is boiled with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934). It is convertible into *β*-chloronaphthalene-3:6-disulphonyl chloride, needles, m.p. 165°, and 2:3:6-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 12).

**Reactions.**—It couples with diazotised bases as end component in azo-dyes. Digestion with 75% caustic soda solution at 230–250° converts it into 2-amino-3-naphthol-6-sulphonic acid.

(v) *β*-Naphthylamine-3:7-disulphonic Acid (*β*-naphthylamine-[δ]-disulphonic acid), is formed when sodium *β*-naphthol-3:7-disulphonate is heated with ammonia and ammonium sulphite under pressure (Badische, G.P. 117471; B.P. 1387, 1900). It is also obtained when *β*-naphthylamine-1:3:7-trisulphonic acid is boiled with dilute mineral acids (Dressel and Kothe, Ber. 1894, 27, 1199).

**Identification.**—The acid barium salt forms very sparingly soluble microscopic crystals, the acid potassium salt, sparingly soluble scales; the acid sodium salt dissolves in 12.5 parts of boiling water, or in 50 parts of water at 20°, the solutions showing blue fluorescence (Dressel and Kothe, *l.c.*). It is convertible into *β*-chloronaphthalene-3:7-disulphonyl chloride, needles, m.p. 176°, and 2:3:6-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 127).

**Reactions.**—It couples with diazotised bases as end component in disazo-dyes. On sulphonation with 40% anhydro-acid at 80–90°, it is converted into  $\beta$ -naphthylamine-1:3:7-trisulphonic acid.

(vi)  $\beta$ -Naphthylamine-4:7-disulphonic Acid (*Andresen's acid*) is obtained when  $\beta$ -nitronaphthalene-4:7-disulphonic acid is reduced (Schultz, Ber. 1890, 23, 77); or (25%) when  $\beta$ -naphthylamine-7-sulphonic acid is sulphonated with 20–25% anhydro-acid in the cold, and, after removal of the 1:7-disulphonic acid as potassium salt, is separated as normal sodium salt from the more soluble 5:7-disulphonate (Bayer, G.P. 79243; Dressel and Kothe, Ber. 1894, 27, 1196; see the 5:7-disulphonic acid).

**Identification.**—The normal barium and sodium salts, crystalline crusts, and the acid sodium salt,  $\text{NaHA} + \text{H}_2\text{O}$ , needles, in dilute solution show intense blue fluorescence (Dressel and Kothe, l.c.). It is convertible into  $\beta$ -chloronaphthalene-4:7-disulphonyl chloride, needles, m.p. 174°, and 1:3:6-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1891, 7, 27).

**Reactions.**—Diazotised, it furnishes  $\beta$ -naphthol-4:7-disulphonic acid when boiled with water. Digestion with 35% caustic potash solution at 180–200° converts it into 2-amino-4-naphthol-7-sulphonic acid. When heated with aniline and aniline hydrochloride at 150–170° it yields 1:3-dianilinonaphthalene-6-sulphonic acid.

(vii)  $\beta$ -Naphthylamine-4:8-disulphonic Acid is obtained by the reduction of  $\beta$ -nitronaphthalene-4:8-disulphonic acid (Cassella, G.P. 65997; Fischer, cf. J.S.C.I. 1898, 17, 837).

**Identification.**—The acid forms prisms; the acid barium salt,  $\text{BaH}_2\text{A}_2$ , minute needles; the acid sodium salt, needles, easily soluble in hot water. The alkaline solutions show deep blue fluorescence. It is convertible into naphthaleno-1:5-disulphonic acid (Cassella, l.c.).

**Reactions.**—It does not couple with diazotised bases (Cassella, l.c.). From its moderately soluble diazo-compound,  $\beta$ -naphthol-4:8-disulphonic acid has been obtained. Fusion with caustic alkali at 215° converts it into 2-amino-4-naphthol-8-sulphonic acid. By digestion with water or 10% sulphuric acid at 180°, it yields  $\beta$ -naphthol-4-sulphonic acid.

When boiled with zinc dust and dilute caustic soda solution it furnishes a mixture of the  $\beta$ -naphthylamine-4- and -8-sulphonic acids (Kalle, G.P. 233934), but with sodium amalgam in the cold the products are  $\beta$ -naphthylamine-8-sulphonic acid (Bayer, G.P. 255724; B.P. 28172, 1911) and  $\beta$ -naphthylamine (Friedländer and Lucht, Ber. 1893, 26, 3033). Nitration converts its acetyl derivative into the 6-nitro-compound (Höchst, G.P.a. 31417). When heated with aniline and aniline hydrochloride at 150–170° it yields 1:3-dianilinonaphthalene-5-sulphonic acid. By sulphonation with 40% anhydro-acid at 80–120°,  $\beta$ -naphthylamine-4:6:8-trisulphonic acid is obtained.

(viii)  $\beta$ -Naphthylamine-5:7-disulphonic Acid.—This acid is formed as the minor product in the preparation of  $\beta$ -naphthylamine-6:8-disulphonic acid by the sulphonation of  $\beta$ -naphthylamine. The sulphonation is carried

out at first in weak oleum at low temperature (65°). All four heteronuclear monosulphonic acids are formed. The sulphonation is carried further with more strong oleum, and at higher temperature (85°) the  $\beta$ -naphthylamine-6-sulphonic acid and the  $\beta$ -naphthylamine-8-sulphonic acid are converted to  $\beta$ -naphthylamine-6:8-disulphonic acid whilst the  $\beta$ -naphthylamine-5- and 7-sulphonic acids become  $\beta$ -naphthylamine-1:5:7-trisulphonic acid. The separation is effected by suitably diluting the sulphonation mass, which precipitates the  $\beta$ -naphthylamine-6:8-disulphonic acid in 44% yield. The filtrate containing the easily soluble trisulphonic acid is heated to 125° to remove the 1-sulphonic acid group. The  $\beta$ -naphthylamine-5:7-sulphonic acid is precipitated on cooling and is obtained in 37% yield (H. E. Fierz-David and L. Blangey, "Farbenchemie," 4th ed. 1938).

The maximum yield of  $\beta$ -naphthylamine-1:5:7-trisulphonic acid is obtained in 15 hours at 95° using oleum containing 12% excess free sulphur trioxide. Yields: 49%  $\beta$ -naphthylamine-6:8-disulphonic acid, 30.5%  $\beta$ -naphthylamine-5:7-disulphonic acid (Ofizerov, Anilino-kras Prom. 1934, 491–497).

**Identification.**—The acid potassium salt is convertible into  $\beta$ -chloronaphthalene-5:7-disulphonyl chloride, prisms, m.p. 166°; and 1:3:6-trichloronaphthalene (Armstrong and Wynne, Proc. C.S. 1890, 6, 131). The solubilities of the acid and some of its salts, expressed as parts per 100 parts of the saturated solution at 20° are as follows:  $\text{H}_2\text{A}, 5\text{H}_2\text{O}$ , 22.97;  $\text{Na}_2\text{A}, 6\text{H}_2\text{O}$ , 72.2;  $\text{NaHA}, 4\text{H}_2\text{O}$ , 7.9;  $\text{K}_2\text{A}, 2\text{H}_2\text{O}$ , 63.9;  $\text{KHA}, 4\text{H}_2\text{O}$ , 2.58;  $\text{MgA}, 8\text{H}_2\text{O}$ , 21.1;  $\text{CaA}, 4\text{H}_2\text{O}$ , 40.2;  $\text{BaA}, 3\text{H}_2\text{O}$ , 22.7;  $\text{ZnA}, 8\text{H}_2\text{O}$ , 39.4;  $\text{PbA}, 6\text{H}_2\text{O}$ , 48.1 (Fierz-David and Braunschweig, Helv. Chim. Acta, 1923, 6, 1146).

**Reactions.**—By the bisulphito method, it furnishes  $\beta$ -naphthol-5:7-disulphonic acid. Digestion with 50% caustic soda solution at 190° converts it into 2-amino-5-naphthol-7-sulphonic acid (J-acid). On sulphonation with 40% anhydro-acid at 100°, it yields  $\beta$ -naphthylamine-1:5:7-trisulphonic acid. When desulphonated by sodium amalgam in the cold,  $\beta$ -naphthylamine-7-sulphonic acid is the product (Bayer, G.P. 255724; B.P. 28172, 1911).

Converted into the toluene-*p*-sulphonyl derivative, it gives the 1-chloro-compound on chlorination, from which 1-chloro-2-amino-5-naphthol-7-sulphonic acid can be prepared.

(ix)  $\beta$ -Naphthylamine-6:8-disulphonic Acid.—The technical preparation of this acid has already been described (see  $\beta$ -naphthylamine-5:7-disulphonic acid). The pure acid can also be obtained from sodium  $\beta$ -naphthol-6:8-disulphonate by heating with ammonia and ammonium sulphite under pressure (Badische, G.P. 117471; B.P. 1387, 1900; Bueherer, J. pr. Chem. 1904, [ii], 70, 358).

**Identification.**—The solubilities of the acid and some of its salts, expressed as parts in 100 parts of the saturated solution at 20°, are as follows:  $\text{H}_2\text{A}, 4\text{H}_2\text{O}$ , 9.24;  $\text{Na}_2\text{A}, 3\text{H}_2\text{O}$ , 59.0;  $\text{NaHA}, 4\text{H}_2\text{O}$ , 7.5;  $\text{K}_2\text{A}, 2\text{H}_2\text{O}$ , 51.6;  $\text{KHA}, 2\text{H}_2\text{O}$ , 2.5;  $\text{MgA}, 8\text{H}_2\text{O}$ , 8.7;  $\text{CaA}, 3\text{H}_2\text{O}$ , 29.1;  $\text{BaA}, 3\text{H}_2\text{O}$ , 12.0;

$\text{ZnA}, 8\text{H}_2\text{O}$ , 34.5;  $\text{PbA}, \text{H}_2\text{O}$ , 44.5 (Fierz-David and Braunschweig, *l.c.*).

It is convertible into  $\beta$ -chloronaphthalene-6:8-disulphonyl chloride, needles, m.p.  $170^\circ$ , and 1:3:7-trichloronaphthalene (Armstrong and Wynne, *Proc. C.S.* 1890, 6, 13).

**Reactions.**—It does not couple with diazotised bases (*cf.* Witt, *Ber.* 1888, 21, 3487). Digestion with 75% caustic soda solution at  $230$ – $250^\circ$  converts it into 2-amino-8-naphthol-6-sulphonic acid (Höchst, G.P. 81281). On sulphonation with 40% anhydro-acid at  $80$ – $90^\circ$ , it yields  $\beta$ -naphthylsulphamino-6:8-disulphonic acid (Dressel and Kothe, *Ber.* 1894, 27, 2153), but at  $120$ – $130^\circ$ ,  $\beta$ -naphthylamine-3:6:8-trisulphonic acid.

#### $\beta$ -NAPHTHYLAMINETRISULPHONIC ACIDS.

(i)  $\beta$ -Naphthylamine-1:3:7-trisulphonic Acid is formed when  $\beta$ -naphthylamine-3:7-disulphonic acid is sulphonated with 40% anhydro-acid at  $80$ – $90^\circ$  (Bayer, G.P.a. 7036; Dressel and Kothe, *Ber.* 1894, 27, 1199); also when  $\beta$ -naphthol-1:3:7-trisulphonic acid is heated with 25% ammonia solution under pressure at  $190^\circ$  (Bayer, G.P.a. 7003; B.P. 17141, 1893; Dressel and Kothe, *l.c.*). The acid barium salt and acid sodium salt,  $\text{Na}_2\text{HA} + 4\text{H}_2\text{O}$ , scales, are easily soluble, and in solution show violet blue fluorescence.

**Reactions.**—When boiled with dilute mineral acid it yields  $\beta$ -naphthylamine-3:7-disulphonic acid. On sulphonation with 40% anhydro-acid at  $130^\circ$ , it is converted into a mixture of the 3:5:7- and 3:6:7-trisulphonic acids with the 1:3:6:7-tetrasulphonic acid.

(ii)  $\beta$ -Naphthylamine-1:5:7-trisulphonic Acid is formed when  $\beta$ -naphthylamine-5-sulphonic, or 1:5-disulphonic, or 5:7-disulphonic acid is sulphonated with 40% anhydro-acid at  $100^\circ$  (Bayer, G.P. 80878; B.P. 20580, 1893).

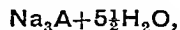
The barium, acid potassium, and acid sodium salts dissolve easily, giving solutions which show fluorescence.

**Reactions.**—It does not couple with diazobenzene chloride (Bayer, *l.c.*). From its easily soluble diazo-compound, the diazo-oxide of 2-amino-1-naphthol-5:7-disulphonic acid is obtained when the solution is rendered alkaline by sodium carbonate (Höchst, G.P.a. 16863; B.P. 23993, 1902). Digestion with 65% caustic soda solution at  $160$ – $220^\circ$  converts it into 2-amino-5-naphthol-1:7-disulphonic acid. By partial hydrolysis with boiling dilute mineral acids it yields  $\beta$ -naphthylamine-5:7-disulphonic acid. When heated with 30% anhydro-acid at  $140$ – $160^\circ$  it undergoes change into the isomeric  $\beta$ -naphthylamine-3:5:7-trisulphonic acid.

(iii)  $\beta$ -Naphthylamine-3:5:7-trisulphonic Acid is formed, together with the 3:6:7-trisulphonic acid and the 1:3:6:7-tetrasulphonic acids, when  $\beta$ -naphthylamine-3:7-disulphonic acid is heated with 40% anhydro-acid at  $130^\circ$ . By boiling the product with water, the tetrasulphonic acid is hydrolysed to the 3:6:7-trisulphonic acid, which is then converted into sodium salt, and, after acidification, separated as the sparingly soluble acid sodium salt. From the concentrated mother-liquor the easily soluble acid sodium salt of the 3:5:7-isomer can

be separated (Bayer, G.P. 81762; B.P. 17141A, 1893; Dressel and Kothe, *Ber.* 1894, 27, 1202). It is the sole product of the change which occurs when  $\beta$ -naphthylamine-1:5:7-trisulphonic acid is heated with 30% anhydro-acid at  $140$ – $160^\circ$  (Bayer, G.P. 90849).

**Identification.**—The sodium salt,



from dilute alcohol, the acid sodium salt,  $\text{Na}_2\text{HA}$ , and the acid barium salt are very soluble, and in solution show intense green fluorescence.

**Reactions.**—From its very soluble diazo-compound,  $\beta$ -naphthol-3:5:7-trisulphonic acid has been obtained (Dressel and Kothe, *l.c.*). Digestion with 30% caustic soda solution at  $190^\circ$  converts it into 2-amino-5-naphthol-3:7-disulphonic acid.

(iv)  $\beta$ -Naphthylamine-3:6:7-trisulphonic Acid is formed when  $\beta$ -naphthylamine-3:7-disulphonic acid is heated with 40% anhydro-acid at  $130^\circ$ , being separated by means of its sparingly soluble acid sodium salt from the 3:5:7-trisulphonic acid also produced (*q.v.*); or when  $\beta$ -naphthylamine-1:3:6:7-tetrasulphonic acid is boiled with dilute mineral acids (Bayer, G.P. 81762; B.P. 17141A, 1893); or when  $\beta$ -naphthol-3:6:7-trisulphonic acid is heated with 25% ammonia solution (3 parts) and ammonium chloride (0.5 part) during 8 hours at 30–40 atm. (Bayer, G.P.a. 7019; B.P. 17141, 1893).

**Identification.**—The sodium salt is easily, the barium salt and acid sodium salt,  $\text{Na}_2\text{HA} + 3\text{H}_2\text{O}$ , long silky needles, are sparingly soluble in cold water, the solutions showing intense blue fluorescence.

**Reactions.**—From its sparingly soluble diazo-compound,  $\beta$ -naphthol-3:6:7-trisulphonic acid has been obtained. Digestion with 55% caustic soda solution at  $180$ – $240^\circ$  converts it into 2-amino-7-naphthol-3:6-disulphonic acid. On sulphonation with 40% anhydro-acid at  $100$ – $130^\circ$ , it yields  $\beta$ -naphthylamine-1:3:6:7-tetrasulphonic acid.

(v)  $\beta$ -Naphthylamine-3:6:8-trisulphonic Acid is obtained when  $\beta$ -naphthol-3:6:8-trisulphonic acid is heated with ammonia at  $200$ – $250^\circ$  (Landshoff, G.P. 27378; *cf.* Dressel and Kothe, *Ber.* 1894, 27, 2154); or when  $\beta$ -naphthylamine-6:8-disulphonic acid is heated with 40% anhydro-acid at  $120$ – $130^\circ$  (Dressel and Kothe, *l.c.*); or when sodium  $\alpha$ -nitronaphthalene-3:6:8-trisulphonate is heated with ammonia solution under pressure at  $150$ – $170^\circ$ , nitrogen being eliminated (Kalle, G.P. 176621).

**Identification.**—The acid potassium salt,  $\text{K}_2\text{HA} + 1\frac{1}{2}\text{H}_2\text{O}$ , forms needles, soluble in 40 parts of water at  $20^\circ$ ; the acid sodium salt, easily soluble needles; the solutions show intense sky-blue fluorescence.

**Reactions.**—Digestion with 80% caustic soda solution at  $220$ – $260^\circ$  converts it into 2-amino-8-naphthol-3:6-disulphonic acid. By desulphonation with zinc dust and boiling dilute caustic soda solution, it yields  $\beta$ -naphthylamine-3:6-disulphonic acid.

(vi)  $\beta$ -Naphthylamine-4:6:8-trisulphonic Acid is obtained when sodium  $\beta$ -naphthylamine-

4:8-disulphonate is heated with 40% anhydro-acid at 80–90°, and finally at 120°.

**Reaction.**—When heated with 60% caustic soda solution at 170–180°, it is converted into 2-amino-4-naphthol-6:8-disulphonic acid (Bayer, G.P.a. 8154; G.P. 89242).

The condensation products corresponding with those obtained from  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid (*q.v.*) have not the same trypanocidal effects (Morgan and Mitchell, J.C.S. 1932, 1910).

#### $\beta$ -NAPHTHYLAMINETETRASULPHONIC ACID.

**$\beta$ -Naphthylamine-1:3:6:7-tetrasulphonic Acid** occurs in the product formed when  $\beta$ -naphthylamine-3:7-disulphonic acid is heated with 40% anhydro-acid at 130° (see the 3:5:7-trisulphonic acid). It is obtained when  $\beta$ -naphthylamine-3:6:7-trisulphonic acid is heated with 40% anhydro-acid at 100–130° (Dressel and Kothe, Ber. 1894, 27, 1203), or when sodium  $\beta$ -naphthol-1:3:6:7-tetrasulphonate is heated with 25% ammonia solution at 180° under pressure (Bayer, G.P.a. 7003; B.P. 17141, 1893; Dressel and Kothe, *l.c.*).

**Salts.**—The barium salt,  $\text{Ba}_2\text{A} \cdot 6\text{H}_2\text{O}$ , sparingly soluble microscopic crystals, and the easily soluble sodium salt show, in dilute solution, violet-blue fluorescence. Acid salts have not been obtained, and acid solutions when boiled undergo partial hydrolysis, giving rise to  $\beta$ -naphthylamine-3:6:7-trisulphonic acid.

#### HALOGENO- $\beta$ -NAPHTHYLAMINES.

The chlorination of  $\beta$ -naphthylamine and its functional derivatives has been comparatively little studied, but more complete investigation of bromination has been made. Bleaching powder oxidises  $\beta$ -naphthylamine to dinaphthazine; chlorination of the sulphate in strong sulphuric acid gives 5:8-dichloro- $\beta$ -naphthylamine, the amino-group having no orientating effect under these conditions. 1-Chloroacet- $\beta$ -naphthalide is obtained by chlorinating acet- $\beta$ -naphthalide. Bromination of acyl or benzylidene derivatives of  $\beta$ -naphthylamine causes bromination successively in the 1-, 6-, and 3-positions, the 1-bromine being readily removed by reduction from the mono-, di-, and tri-bromo-compounds.

1-Chloro- $\beta$ -naphthylamine obtained by chlorinating acet- $\beta$ -naphthalide in acetic acid solution, and hydrolysing the product with hot hydrochloric acid, forms needles, m.p. 59°. The hydrochloride,  $\text{B} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , forms needles; the acetyl derivative, needles, m.p. 147° (Clevo, Ber. 1887, 20, 1889).

1-Chloro- $\beta$ -naphthylaminesulphonic Acids.—When sulphonated with 2% anhydro-acid at 70°, 100°, and 160°, 1-chloro- $\beta$ -naphthylamine yields as chief product respectively the 5-, 6-, and 7-sulphonic acids (Armstrong and Wynne, Proc. C.S. 1889, 5, 36, 48). These acids when diazotised and heated in solution with excess of sodium carbonate at 50–60°, are converted into the diazo-oxides of the corresponding 2-amino- $\alpha$ -naphtholsulphonic acids (Badisch, G.P. 145906; 148882; B.P. 6615, 1902).

4-Chloro- $\beta$ -naphthylamine, m.p. 68°, has

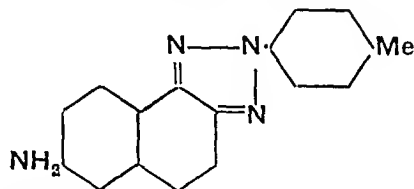
been prepared starting from 2-nitro-1-naphthylamine (Hodgson and Elliott, J.C.S. 1935, 1850).

**Bromo- $\beta$ -naphthylamines.**—The bromination of  $\beta$ -naphthylamine (in the form of functional derivatives) has been studied by Franzen and collaborators (J. pr. Chem. [ii], 1913, 88, 755; 1917, 95, 160; 1921, 101, 69) and the following have been described: 1-bromo- $\beta$ -naphthylamine, m.p. 63° (acetyl, m.p. 140°); 6-bromo- $\beta$ -naphthylamine, m.p. 128° (acetyl, m.p. 192°); 1:6-dibromo- $\beta$ -naphthylamine, m.p. 119–120°; 3:6-dibromo- $\beta$ -naphthylamine, m.p. 187° (acetyl, m.p. 195°); 4-bromo- $\beta$ -naphthylamine has m.p. 71.5° (acetyl, m.p. 189°) (Fries and Schimmolschmidt, Annalen, 1930, 484, 269) and 5-(or 8-)-bromo- $\beta$ -naphthylamine, m.p. 35° (acetyl, m.p. 158°) (von Braun *et al.*, Ber. 1922, 55 [B], 1698).

#### NITRO- $\beta$ -NAPHTHYLAMINES.

Nitration of  $\beta$ -naphthylamine in sulphuric acid gives the 5- and 8-mononitro derivatives, but when acyl derivatives of the base are nitrated a different course is followed. Thus acet- $\beta$ -naphthalide gives first mainly the 1-nitro (about 60%) along with the 6- and 8-nitro derivatives (about 15% each), and on dinitration the 1:5- and 1:8-dinitro derivatives (Vesely and Jakeš, Bull. Soc. chim. 1923, [iv], 83, 942) and some 1:6-dinitro derivative (Bell, J.C.S. 1929, 2784). When, however, *p*-toluenesulphon- $\beta$ -naphthalide is nitrated, the 1-nitro-derivative is first formed, and by further nitration only the 1:6-dinitro-compound (Morgan and Micklewait, *ibid.* 1912, 101, 148; Bell, *l.c.*). Bell obtained the 1:5 and 1:8-dinitro derivatives by nitrating respectively 5- and 8-nitro-*p*-toluenesulphon- $\beta$ -naphthalide. He found that nitration of *m*-nitrobenzenesulphon- $\beta$ -naphthalide gave successively the 1:6-dinitro and 1:6:8-trinitro-derivatives. When *N*- $\beta$ -naphthyl-*N'*-ethyl-carbamido or methyl  $\beta$ -naphthylcarbamate is nitrated, 1-, 6-, and 8-nitro derivatives are formed, followed by 1:6- and 1:8-di- and finally 1:6:8-tri-nitro derivatives (Groeneveld, Rec. trav. chim. 1932, 51, 783).

5- and 8-Nitro- $\beta$ -naphthylamines when coupled with diazo-compounds form 1-azo derivatives which on oxidation give nitronaphthatriazoles, reducible to aminonaphthatriazoles such as



Such compounds have been patented as azo-dyo intermediates (Holliday and Morgan, B.P. 191797; Morgan and Chazan, J.S.C.I. 1922, 41, 1r; Morgan and Gilmour, *ibid.*, p. 61r). Morgan and Jones have also described condensation products of 1-, 5-, and 8-nitro- $\beta$ -naphthylamine with formaldehyde (*ibid.* 1923, 42, 92r).

The nitration of  $\beta$ -naphthylamine-6-sulphonic acid (Brönner's acid) to the 8-nitro-derivative and of  $\beta$ -naphthylamine-4:8-disulphonic acid (amino-C-acid) to the 6-nitro-derivative have



been carried out by Voroschcov and Gribov (A. 1923, i, 919).

Vesely and Dvřak, by nitrating 1-bromoacet- $\beta$ -naphthalide obtained 1:8-dinitroacet- $\beta$ -naphthalide with some 5-nitro-1-bromoacet- $\beta$ -naphthalide. Both 6- and 8-nitroacet- $\beta$ -naphthalide brominate in the 1-position (Chem. Listy, 1923, 17, 163). The colour of the nitronaphthylamines in relation to their possible structure has been discussed by Hodgson and H. S. Turner (J. Soc. Dyers and Col. 1943, 59, 218).

(i) 1-Nitro- $\beta$ -naphthylamine.—The preparation of this compound by nitrating acet- $\beta$ -naphthalide in acetic acid is described by Heilpern and Spielfogel (J.S.C.I. 1898, 17, 836). Vesely and Jakeš used acetic anhydride as medium. They dissolved 30 g. of acet- $\beta$ -naphthalide in 40 g. of warm acetic anhydride, and after cooling added 20 g. of 60% nitric acid to the fine suspension, at 25–30°. The whole was then dissolved by warming, cooled and seeded with 1-nitroacet- $\beta$ -naphthalide. The mass of crystals separating was filtered and recrystallised from alcohol. 1-Nitroacet- $\beta$ -naphthalide has m.p. 126°; 1-nitro- $\beta$ -naphthylamine obtained by hydrolysing the acetyl compound forms orange-yellow crystals, m.p. 126–127° (Bull. Soc. chim. 1923, [iv], 33, 942). From its diazonium compound Voroschcov has prepared 1-nitronaphthalenesulphinic acid (J. Gen. Chem. Russ. 1939, 522). By mercuric acetate it is converted into the 3-mercuriacetate, whence 3-iodo-1-nitro-2-naphthylamine is obtained (Hodgson and Elliott, J.C.S. 1939, 345).

1-Nitroacet- $\beta$ -naphthalide gives 1-nitro- $\beta$ -naphthol when boiled with aqueous caustic soda (Jacobson, Ber. 1881, 14, 1792).

(ii) 3-Nitro- $\beta$ -naphthylamine is obtained by reduction of 2:3-dinitronaphthalene with sodium sulphide in methyl alcohol in presence of sodium bicarbonate. It forms red needles, m.p. 86.5°; *picrate*, m.p. 171–172°; *acetyl* derivative, m.p. 191.5–192.5° (Hodgson and H. S. Turner, J.C.S. 1943, 636). The base is soluble in dilute hydrochloric acid.

(iii) 4-Nitro- $\beta$ -naphthylamine is produced together with 3-nitro-1-naphthylamine (*q.v.*) when 1:3-dinitronaphthalene is reduced. It crystallises from 50% aqueous alcohol in red needles, m.p. 98.5° (Hodgson and Hathway, *ibid.* 1944, 386); *formyl* derivative, m.p. 205°; *acetyl* derivative, m.p. 241° (Hodgson and Birtwell, *ibid.* 1944, 76).

(iv) 5-Nitro- $\beta$ -naphthylamine is formed as chief product, together with the 8-isomer, when  $\beta$ -naphthylamine nitrate (1 part) is stirred into monohydrate (4 parts) at 0°, 20% anhydro-acid (2 parts) being added gradually during the operation, and separates in the cold as sulphate when the nitration product is diluted with water (50 parts), the more soluble sulphate of the 8-isomer being retained in the mother-liquor (Hirsch, G.P. 57491; B.P. 9768, 1890; Friedländer and Szymanski, Ber. 1892, 25, 2076). It forms red needles, m.p. 143.5°; its *acetyl* derivative yellow needles, m.p. 185.5°; *p-toluenesulphonyl* derivative, m.p. 158° (Bell, *l.c.*).

*Reactions.*—From its diazo-compound 5-nitro- $\beta$ -naphthol has been obtained. By reduction

with iron and acetic acid it yields 1:6-diamino-naphthalene (Friedländer and Szymanski, *l.c.*); but when boiled with sodium sulphite or bisulphite solution it is converted into a 1:6-diamino-naphthalenesulphonic acid (Read, Holliday and Sons, B.P. 26020, 1896).

(v) 6-Nitro- $\beta$ -naphthylamine, orange flakes, m.p. 203°; *acetyl* derivative, yellow needles, m.p. 224° (Vesely and Jakeš, Bull. Soc. chim. 1923, [iv], 33, 942). It forms 6-nitro-2-naphthylarsinic acid (Sweet and Hamilton, J. Amer. Chem. Soc. 1934, 56, 2408).

6-Nitro- $\beta$ -naphthylamine-8-sulphonic Acid, obtained by nitrating  $\beta$ -naphthylamine-8-sulphonic acid dissolved in sulphuric acid (Immerheiser, G.P. 57023), gives a *barium* salt,  $\text{BaA}_2 + 4\frac{1}{2}\text{H}_2\text{O}$ , and *ammonium* salt,  $\text{NH}_4\text{A}$ , in red crystals (Jacchia, Annalen, 1902, 323, 119), and yields 2:6-diaminonaphthalene on reduction with sodium amalgam (Friedländer and Lucht, Ber. 1893, 26, 3033).

The 4:8-disulphonic acid is obtained by nitrating acet- $\beta$ -naphthalide-4:8-disulphonic acid in sulphuric acid solution and hydrolysing the product (Höchst, G.P.a. 31417).

(vi) 7-Nitro- $\beta$ -naphthylamine, m.p. 184.5°, is obtained by mono-reduction of 2:7-dinitronaphthalene (Hodgson and Ward, J.C.S. 1945, 590).

(vii) 8-Nitro- $\beta$ -naphthylamine (*see* 5-nitro- $\beta$ -naphthylamine) forms red needles, m.p. 103.5°, and its *acetyl* derivative, yellow needles, m.p. 195.5°; *p-toluenesulphonyl* derivative, m.p. 139° (Bell, *l.c.*). From its diazo-compound 8-nitro- $\beta$ -naphthol can be obtained, and it gives 1:7-diaminonaphthalene on reduction (Friedländer and Szymanski, *ibid.* 1892, 25, 2081).

(viii) 1:5-Dinitro- $\beta$ -naphthylamine has m.p. 191°; it is yellow in colour; *acetyl* derivative, m.p. 200–201° (Vesely and Jakeš, *l.c.*); *p-toluenesulphonyl* derivative, m.p. 182° (Bell, *l.c.*).

(ix) 1:6-Dinitro- $\beta$ -naphthylamine, m.p. 246°, gives an *acetyl* derivative, m.p. 230° (Bell, *l.c.*).

(x) 1:8-Dinitro- $\beta$ -naphthylamine forms both yellow and orange crystals, m.p. 221–222°; *acetyl* derivative, m.p. 237–238° (Groeneveld, *l.c.*); *p-toluenesulphonyl* derivative, m.p. 221° (Bell, *l.c.*).

(xi) 1:6:8-Trinitro- $\beta$ -naphthylamine, m.p. 300° (decomp.), is described by Bell (*l.c.*).

## DIAMINONAPHTHALENES.

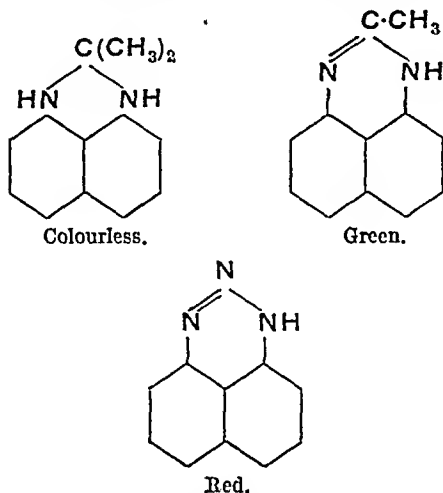
The ten possible diaminonaphthalenes are all known. The methods employed in their production involve usually either replacement of hydroxyl by amino- in aminonaphthols or dihydroxynaphthalenes, or reduction of dinitronaphthalenes or nitronaphthylamines or of azo-dyes. They are not in themselves technically important except for the identification of azo-dye components.

For the preparation of the 1:2- or 1:4-diamino-naphthalene, reduction of the *o*- or *p*-azo-dyes of the naphthalene series by stannous chloride can be employed; and for that of the 1:3-derivative use is made of the naphthylamine- or naphthol-3-sulphonic acids, as these exchange



the sulphonic-group in the *meta*-position for an amino-group when heated with ammonia. These homonuclear compounds respectively resemble in properties the *ortho*-, *para*-, and *meta*-diamines of the benzene series.

Of the heteronuclear compounds, the 1:5 derivative has been used for the production of disazo-dyes, but the interest attaching to the 1:8-derivative is due less to its property of coupling with diazotised bases than to the readiness with which—like the 1:2- and 2:3-diamines—it forms a third six-membered ring. Some of these *peri*-condensation products are coloured, others colourless, and, according to Sachs, colour or its absence is associated with the presence or absence of an unsaturated linking in the new ring (Annalen, 1909, 365, 53):



The diaminonaphthalenes crystallise well, but, as a rule, are less stable, and therefore less suitable for the production of dyestuffs, than the respective diaminonaphthalenesulphonic acids. With nitrous acid, the 1:2-, 2:3-, and 1:8-diamines furnish azimino-compounds, but the 1:4-diamine is oxidised to [α]-naphthaquinone; the heteronuclear diamines other than the 1:8-isomer give tetrazo derivatives, of which that from the 1:5-diamine furnishes substantive disazo dyes for cotton (Badische, G.P. 39954).

Voroshcov (A. 1922, i, 956) considers that the analogues of benzidine in the naphthalene series are the 1:4-, 1:5-, 1:6-, and 2:6-diaminonaphthalenes which likewise furnish substantive azo-dyes. Substantive azo-dyes have also been obtained from the diacetoacetyl derivatives of the 1:4-, 1:5-, and 2:6-diaminonaphthalenes—these melt respectively at 197°, 249–250°, and 203–204° with decomposition (Griesheim, B.P. 211772).

(i) 1:2-Diaminonaphthalene is obtained by reducing azo-compounds derived from β-naphthylamine by coupling with diazotised bases (Griess, Ber. 1882, 15, 2193; Lawson, *ibid.* 1885, 18, 800, 2423; Sachs, *ibid.*, p. 3128; Witt, *ibid.* 1886, 19, 2795; 1888, 21, 3482); or [β]-naphthaquinonedioxime (Koreff, *ibid.* 1886, 19, 179); or 2-nitro-α-naphthylamine (Lellmann and Remy, *ibid.*, p. 803); or 1-nitro-β-naphthylamine (Lawson, *l.c.*; Lellmann and Remy, *l.c.*) with stannous chloride in hydrochloric acid solution. It can also be obtained

from 1:2-diaminonaphthalene-4-sulphonic acid (Friedländer and Kielbasinski, *ibid.* 1896, 29, 1978) or 3- or 5-sulphonic acid (Gattermann and Schultze, *ibid.* 1897, 30, 53, 55) by interaction with sodium amalgam.

**Preparation.**—On the laboratory scale, 10 g. of benzeneazo-β-naphthylamine, dissolved in 300 g. of boiling dilute acetic acid (1:5), are reduced by adding zinc dust in small quantities until the colour of the solution changes to bright yellow. The sulphate, obtained by filtering the boiling solution into dilute sulphuric acid, is then boiled with sodium carbonate solution until dissolved (Bamberger and Schieffelin, *ibid.* 1889, 22, 1376).

**Identification.**—It separates from hot water in silvery rhombic scales, m.p. 95–96°, and is oxidised rapidly, becoming brown on exposure to the air. The *hydrochloride*, B, 2HCl, forms short prisms easily soluble in water, and with ferric chloride gives an olive-green coloration, changing to brown and yellow; the *sulphate*, B<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub>, scales; the *diacetyl*-compound, needles, m.p. 234° (Lawson, *l.c.*). With benzil, [β]-naphthaquinone, phenanthraquinone (Lawson, *l.c.*; Witt, *l.c.*), or glyoxal (Hinsberg, Ber. 1890, 23, 1394), it yields *quinoxalines*, and with nitrous acid a mixture of the two *azimino*-compounds (Morgan and Godden, J.C.S. 1910, 97, 1718).

The 1-*acetyl* derivative has been obtained, not by acetylation but mixed with the 1:4-compound (*q.v.*), by nitration of acet-α-naphthalide and reduction of the product (G.P.a. 6503).

2-*Phenylamino*-α-naphthylamine, broad needles or scales, m.p. 138–140°, forming very sparingly soluble salts (Witt, *ibid.* 1887, 20, 573, 1184; Zincke and Lawson, *ibid.*, p. 1170); and the 2-*p-tolyl* derivative, needles, m.p. 146–147° (Fischer, *ibid.* 1892, 25, 2846), have been obtained by reduction of azo derivatives of phenyl- and *p*-tolyl-β-naphthylamine.

(ii) 1:3-Diaminonaphthalene is formed when 1:3-dinitronaphthalene is reduced with tin and hydrochloric acid (Urban, *ibid.* 1887, 20, 973). It is also produced when sodium α-naphthylamine- or α-naphthol-3-sulphonate is heated with ammonium chloride and 22% ammonia under pressure at 160–180° (Kalle, G.P. 89061; B.P. 9103, 1895); or when 1-amino-3-naphthol (Friedländer, Ber. 1895, 28, 1953) or 1:3-dihydroxynaphthalene (Friedländer and Rüdte, *ibid.* 1896, 29, 1612) is heated with concentrated aqueous ammonia under pressure at 160°.

**Identification.**—It crystallises from water in scales, m.p. 96°; its *hydrochloride*, B, 2HCl, and *sulphate*, in easily soluble needles, which in solution give a dark brown coloration with ferric chloride; the *diacetyl* compound in sparingly soluble needles, m.p. 263° (Friedländer, *l.c.*). With diazotised bases it gives *chrysoïdines*, and with nitrous acid a deep yellow coloration (Urban, *l.c.*).

1:3-Dianilinonaphthalene is obtained when α-naphthylamine-3-sulphonic acid (Bayer, G.P. 75296; B.P. 8898, 1893), phenyl-α-naphthylamine-3-sulphonic acid (Bayer, G.P. 78854; B.P. 19623, 1893), or α-naphthol-3-sulphonic acid (Bayer, G.P. 77866; B.P. 16780, 1893) is heated

with aniline and aniline hydrochloride at 150–170°. It is insoluble in and its hydrochloride is decomposed by water. The corresponding ditolyl, dixylyl, and phenyltolyl derivatives have also been prepared.

(iii) 1:4-Diaminonaphthalene is formed by reducing azo derivatives of  $\alpha$ -naphthylamine with tin or stannous chloride and hydrochloric acid (Perkin, J.C.S. 1865, 18, 173; Griess, Ber. 1882, 15, 2192; Friedländer, *ibid.* 1889, 22, 590) or with sodium hydrosulphite (Grandmougin, *ibid.* 1906, 39, 3561); or by reducing 4-nitro- $\alpha$ -naphthylamine with tin and hydrochloric acid (Liebermann and Dittler, Annalen, 1876, 183, 238). It is also formed by hydrolysing 1:4-diaminonaphthalene-6-sulphonic acid (Casella, G.P. 74177; B.P. 15444, 1893).

**Preparation.**—On the laboratory scale, benzeneazo- $\alpha$ -naphthylamine is boiled with zinc dust and water, the colourless solution filtered into dilute sulphuric acid, and the crystalline sulphate warmed with aqueous sodium carbonate for about 5 minutes (Bamberger and Schieffelin, Ber. 1889, 22, 1381).

**Identification.**—It crystallises from water in needles or small prisms, m.p. 120°, which when moist rapidly become coloured green and decompose. The hydrochloride,  $B, 2HCl$ , forms readily soluble scales, and in neutral solution with ferric chloride gives a green coloration, changing to a brown precipitate of impure  $[\alpha]$ -naphthaquinone (Griess, l.c.); the sulphate,  $B, H_2SO_4$ , sparingly soluble needles; the diacetyl derivative, needles, m.p. 305° (Kleemann, *ibid.* 1886, 19, 334; Bamberger and Schieffelin, l.c.).

**Reactions.**—By nitrous acid (Grandmougin and Michel, *ibid.* 1892, 25, 977) or by dilute chromic acid solution, or ferric chloride, it is oxidised to  $[\alpha]$ -naphthaquinone.

**Monoacetyl-1:4-diaminonaphthalene** is obtained, mixed with the 1:2-derivative, when acet- $\alpha$ -naphthalide is stirred with four times its weight of 40% nitric acid at 0° during about 18 hours and the product reduced by iron. To separate the isomers, the mixture (1 mol.) is either heated with dilute hydrochloric acid (1 mol.) at 80° when the hydrochloride of the 1:4-derivative passes completely into solution and can afterwards be salted out, or boiled with dilute sulphuric acid ( $\frac{1}{2}$  mol.) when the sulphate, being only sparingly soluble in the cold, can be freed from the 1:2-derivative which remains in solution (Dahl, G.P.a. 6503). Unlike the diamine, which is not diazotisable, this compound can be used in the production of disazo-dyes, as the free amino-group can be diazotised and coupled before the acetyl-amino-group is deacetylated.

(iv) 1:5-Diaminonaphthalene ( $[\alpha]$ -diaminonaphthalene; semi-naphthalidam) is obtained from 1:5-dinitronaphthalene by reduction. It is also formed when 1:5-dihydroxynaphthalene is heated with ammonium bisulphite solution and ammonia at 125° (Badische, G.P. 117471; B.P. 1387, 1900); or when 1:5-diaminonaphthalene-2-sulphonic acid is heated with dilute mineral acid (Friedländer and Kielbasinski, Ber. 1896, 20, 1983); or when  $\alpha$ -naphthylamine is heated with naphthalene and sodamide at 230° (Sachs, *ibid.* 1906, 39, 3021).

**Identification.**—It crystallises in needles, m.p. 189.5°, sublimes without decomposition, and with ferric chloride gives an intense bluish-violet coloration. The hydrochloride,  $B, 2HCl$ , and the sulphate,  $B, H_2SO_4$ , form moderately soluble needles; the monoacetyl compound has m.p. 164° (Ruggli and Knapp, Helv. Chim. Acta, 1930, 13, 763); the diacetyl compound, m.p. 360°, unlike the diamine, causes serious irritation of the skin (Kunckell and Schneider, Chem.-Ztg. 1912, 36, 1021, 1226; cf. Chem. Fabr. R. Scheuble & Co., *ibid.*, p. 1226). It is convertible into 1:5-dichloronaphthalene (Erdmann, Annalen, 1888, 247, 360).

**Reactions.**—With nitrous acid it yields a tetrazo-compound, and, by coupling with diazotised bases, azo- or disazo-dyes. By the bisulphite reaction, 1-amino-5-naphthol is the product. On sulphonation, its sulphate yields 1:5-diaminonaphthalene-2-sulphonic acid.

(v) 1:6-Diaminonaphthalene, prepared by heating 1:6-dihydroxynaphthalene with ammonia under pressure at 150–300° (Ewer and Pick, G.P. 45788), or  $\beta$ -naphthylamine with sodamide and naphthalene at 230° (Sachs, Ber. 1906, 39, 3022), can be obtained pure by reducing either 5-nitro- $\beta$ -naphthylamine with iron and acetic acid (Friedländer and Szymanski, *ibid.* 1892, 25, 2080; cf. Hirsch, G.P. 57491; Dawson and Hirsch, B.P. 9768, 1890), or 1:6-dinitronaphthalene with tin and hydrochloric acid (Kehrmann and Matis, Ber. 1898, 31, 2419).

**Identification.**—It crystallises from water in short needles, m.p. 77.5°, darkens on exposure to air, shows blue fluorescence in solution, and gives with ferric chloride a dark brownish-violet coloration. The hydrochloride, needles, is easily, but the sulphate,  $B, H_2SO_4$ , needles, only sparingly soluble in water; the diacetyl derivative needles, m.p. 257°, dissolves sparingly in alcohol. The tetrazo-compound is convertible into 1:6-dichloronaphthalene (Friedländer and Szymanski, l.c.).

(vi) 1:7-Diaminonaphthalene is prepared by reducing 8-nitro- $\beta$ -naphthylamine in alcoholic solution with tin and hydrochloric acid (Friedländer and Szymanski, *ibid.* 1892, 25, 2082), or by heating 1:7-dihydroxy- $\beta$ -naphthoic acid with ammonia under pressure at 200–210° (Friedländer and Zinberg, *ibid.* 1896, 29, 40).

**Identification.**—It crystallises from water in needles, m.p. 117.5°, gives with ferric chloride a violet coloration, and forms a diacetyl derivative, rhombohedra, m.p. 213°. The tetrazo-compound is convertible into 1:7-dichloronaphthalene (Friedländer and Szymanski, l.c.).

(vii) 1:8-Diaminonaphthalene (perinaphthylenediamine) can be obtained by reducing 1:8-dinitronaphthalene with tin and hydrochloric acid (Ladenburg, *ibid.* 1878, 11, 1651; Erdmann, Annalen, 1888, 247, 363). It is also formed when 1:8-dihydroxynaphthalene is heated with ammonia under pressure at 250–300° (Erdmann, l.c.).

**Identification.**—It crystallises from aqueous alcohol in needles, m.p. 67°, and in aqueous solution gives, with ferric chloride, a dark chestnut-brown coloration. The hydrochloride,

$B_2HCl$ , forms very soluble scales, m.p.  $280^\circ$  (Ekstrand, Ber. 1887, 20, 1353); the *sulphate*,  $B_2H_2SO_4$ , sparingly soluble needles; the *dibenzoyl* derivative, needles, m.p.  $311-312^\circ$  (Sachs, *ibid.* 1906, 39, 3027); and the *oxalate*, either needles, m.p.  $271^\circ$  (Meyer and Müller, *ibid.* 1897, 30, 775), or  $BA+2H_2O$ , decomp.  $270^\circ$ ;  $B_2A$ , m.p.  $205^\circ$  (Sachs, Annalen, 1909, 365, 101).

**Reactions.**—Many condensation products can be obtained from this diamine. For example, with acetic anhydride it forms a green *anhydro*-compound, m.p.  $210^\circ$  (Sachs, Ber. 1906, 39, 3027); with ethyl oxalate, a red crystalline "*perimidine*" derivative (Aguiar, *ibid.* 1874, 7, 306; Meyer and Müller, *l.c.*; Sachs, *ibid.* pp. 69, 96); with phthalic anhydride a yellow *perimidybenzoic acid* or red *phthaloperinone*, needles, m.p.  $227-228^\circ$  (Sachs, *ibid.*, p. 117; Bayer, G.P. 202354; B.P. 7575, 1908); with acetone a colourless *dimethyldihydroperimidine* (cf. Sachs, *ibid.*, p. 151; Badische, G.P. 122475); with phosgene or alkyl carbonates, colourless *perimidones* (Sachs, *ibid.*, p. 135).

With nitrous acid, it yields a red *azimino* derivative, and can be converted into a *tetrazo*-compound (Ruggli, Helv. Chim. Acta, 1935, 18, 1414). Its *acid sulphate*, when baked in a vacuum, is converted into 1:8-diaminonaphthalene-4-sulphonic acid. Boiled with sodium bisulphite solution and afterwards with alkali, it gives 1-amino-8-naphthol; but when heated with 17% hydrochloric acid at  $180^\circ$  the product is 1:8-dihydroxynaphthalene.

It has been claimed as a rubber preservative (Goodrich, U.S.P. 1532398).

(viii) 2:3 - Diaminonaphthalene is obtained by heating 2:3-dihydroxynaphthalene with 30% ammonium sulphite solution and 20% ammonia at  $80^\circ$ , the product afterwards being acidified (Badische, G.P. 117471; B.P. 1387, 1900; see Goldstein and Streuli, Helv. Chim. Acta, 1937, 20, 520).

**Identification.**—It crystallises from water in scales, m.p.  $191^\circ$ , and gives no coloration with ferric chloride. The hydrochloride is easily, but the sulphate only sparingly, soluble. The *diacetyl* derivative forms needles, m.p.  $247^\circ$ , convertible by prolonged boiling with acetic acid into an *anhydride*, m.p.  $168^\circ$ .

**Reactions.**—Its behaviour is that of an *o*-diamine. With nitrous acid it yields an *azimino* derivative, yellow needles, m.p.  $187^\circ$ , and with diazotised bases (1 mol.) it couples giving red azo-dyes (Friedländer and Zahrzewski, Ber. 1894, 27, 764).

The *diphenyl* derivative obtained by heating 2:3-dihydroxynaphthalene and aniline with 1% of iodine at  $200^\circ$ , forms needles, m.p.  $143^\circ$  (Knoevenagel, J. pr. Chem. 1914, [ii], 89, 37).

(ix) 2:6-Diaminonaphthalene is obtained when 2:6-dihydroxynaphthalene is heated with ammonia-calcium chloride at  $270^\circ$  (Jacchia, Annalen, 1902, 323, 132). It is also formed by reduction of 2:6-diaminonaphthalene-4-sulphonic acid with sodium amalgam (Friedländer and Lucht, Ber. 1893, 26, 3033).

**Identification.**—It crystallises in scales, m.p.  $216^\circ$ , darkens on exposure to the air, and with ferric chloride gives a green coloration, which

changes to blue when the solution is warmed. The *sulphate* is sparingly soluble; the *diacetyl* derivative forms needles.

The *diphenyl* derivative, obtained by heating 2:6-dihydroxynaphthalene with aniline and aniline hydrochloride at  $170^\circ$ , melts at  $210^\circ$  (Leonhardt, G.P. 54087; B.P. 3098, 1890).

(x) 2:7-Diaminonaphthalene is obtained when 2:7-dihydroxynaphthalene is boiled with ammonium sulphite solution and ammonia (Franzen and Deibel, J. pr. Chem. 1908, [ii], 78, 155). It is also formed from 2-amino-7-naphthol by the bisulphite reaction (Bucherer, *ibid.* 1904, [ii], 69, 80).

**Identification.**—It crystallises from water in scales, m.p.  $161^\circ$ , and gives no coloration with ferric chloride. Its salts are easily soluble. The *diacetyl* derivative forms needles, m.p.  $254^\circ$ .

**Reactions.**—Diazotised in acetic acid solution, it yields only a *diazo*-compound (Kaufler and Karrer, Ber. 1907, 40, 3263), but in sulphuric acid a *tetrazo*-derivative convertible into 2:7-dichloronaphthalene (Morgan and Micklethwait, J.C.S., 1910, 97, 2558). By the bisulphite reaction it furnishes 2-amino-7-naphthol.

2:7-Dianilinonaphthalene, obtained when 2:7-dihydroxynaphthalene is heated with aniline and aniline hydrochloride at  $140-180^\circ$  (Durand and Huguenin, G.P. 40886; Annaheim, B.P. 14283, 1886; Ber. 1887, 20, 1372), forms scales, m.p.  $163-164^\circ$ ; its *diacetyl* derivative, small crystals, m.p.  $197.5^\circ$  (Clausius, *ibid.* 1890, 23, 528).

The *o*-tolyl, m.p.  $106^\circ$ ; *p*-tolyl, m.p.  $236-237^\circ$ ; and *m*-xyl, m.p.  $130^\circ$ , derivatives have also been prepared (Durand and Huguenin, *l.c.*).

#### DIAMINONAPHTHALENESULPHONIC ACIDS.

The methods by which sulphonic acids of the heteronuclear diaminonaphthalenes can be obtained do not lend themselves to generalisation; those for the production of homonuclear diaminonaphthalenesulphonic acids can be summarised:

1. For 1:2- or 1:4-diaminonaphthalenesulphonic acids: reduction of azo-dyes formed by coupling diazotised bases with the appropriate  $\beta$ - or  $\alpha$ -naphthylamine-sulphonic acids (cf. Witt, *ibid.* 1888, 21, 3485; Reverdin and de la Harpe, *ibid.* 1892, 25, 1403; 1893, 26, 1281).

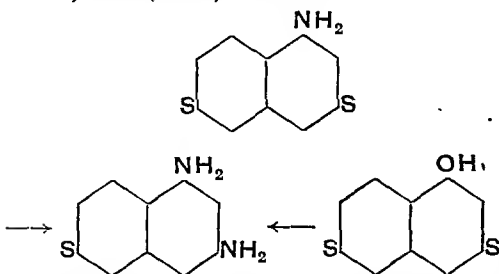
When as may be the case with azo-dyes obtained by coupling with  $\alpha$ -naphthylamine-3- or 5-sulphonic acid, a mixture of the 1:2- and 1:4-diaminonaphthalenesulphonic acids is obtained, the ready solubility of the 1:2 derivative in sodium sulphite solution in the cold affords a convenient means for achieving their separation (Gattermann and Liebermann, Annalen, 1912, 393, 206).

2. For 1:3 - diaminonaphthalenesulphonic acids: interaction of  $\alpha$ -naphthylamine- or  $\alpha$ -naphthol-3-sulphonic acids with ammonia at high temperatures (Kalle, G.P. 89061; B.P. 9103, 1895) (formulae on p. 328a).

Diaminonaphthalenesulphonic acids have been used to a limited extent for the production of azo-dyes and their diaryl derivatives for the manufacture of wool dyes of the azine series.

**For Azo-dyes.**—Diaminonaphthalenesulphonic acids yield azo-dyes, by coupling with di-

azotised bases if derived from the 1:5-, and 2:7-diamines. Like the base itself, 1:5-diaminonaphthalene-3:7-disulphonic acid furnishes a tetrazo-compound which, when coupled, gives direct cotton dyes (Cassella, G.P. 62075; B.P. 15346; 15347, 1890).



1:4-Diaminonaphthalenesulphonic acids do not couple with diazotised bases. By nitrous acid, they are usually oxidised, but azo-dyes can be made from them by employing the mono-acetyl derivatives in which the one amino-group can be diazotised and coupled before the other is deacetylated (*cf.* Cassella, G.P. 78831; 79910; B.P. 15444, 1893). The 2-sulphonic acid can be diazotised in acetic or oxalic acid solution, but only one amino-group is attacked until the product has been coupled with a naphthol, when the second becomes reactive, and by coupling furnishes substantive disazo-dyes for cotton

(Levinstein, G.P. 102160; B.P. 2946, 17064, 1896).

1:8-Diaminonaphthalenesulphonic acids form azimino derivatives with nitrous acid. They couple with diazotised bases forming azo-dyes, but a marked increase in fastness and purity of shade is obtained if instead of the diamino-acids their acetone condensation products (dimethyldi-hydroperimidines) are used (Badische, G.P. 121228; 122475; B.P. 12819, 1900), or if the azo-dyes, formed by coupling 1:8-diaminonaphthalenesulphonic acids with diazotised bases, are converted into azimino derivatives (Cassella, G.P. 77425; B.P. 24714, 1893; G.P. 139908; B.P. 26147, 1901; Bayer, G.P. 222928; *cf.* Höchst, G.P. 143387; B.P. 953, 1903).

*For Azines.*—The sulphonic acids employed in the production of azine dyes are those derived from the diaryl-1:3-diaminonaphthalenes (Bayer, G.P. 78497; 77189; 80778; 86223; 86224; B.P. 8898; 11892, 1893), and from the diaryl-2:6- and diaryl-2:7-diaminonaphthalenes (Leonhardt, G.P. 54087; B.P. 3098, 1890). Of these the 1:3-dianilinnaphthalene-8-sulphonic acid is the most important.

The sources and general characters of diaminonaphthalenesulphonic acids are summarised in the following tables, references to fluorescence, usually green in colour, or non-fluorescence of solutions of the alkali salts being omitted.

#### DIAMINONAPHTHALENEMONOSULPHONIC ACIDS.

Constitution.	Preparation.	Acids, salts, and reactions.
N:N:5 1:2:3	Reduction of azo derivatives of $\alpha$ -naphthylamine-3-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 54).	<i>Acid</i> , HA, broad needles. Gives intense emerald-green coloration with ferric chloride.
1:2:4	Reduction of azo derivatives of $\alpha$ -naphthylamine-4-sulphonic acid (Witt, <i>ibid.</i> 1886, 19, 1720); or of Congo Red (Friedländer and Kielbasinski, <i>ibid.</i> 1896, 29, 1978).	<i>Acid</i> , sparingly soluble needles. Is decomposed by nitrous acid and does not couple. <i>Acetyl</i> derivative converted into <i>ethenyl</i> -compound by mineral acids or heat (Lange, G.P. 57942).
1:2:5	Reduction of azo derivatives of $\alpha$ -naphthylamine-5-sulphonic acid (Gattermann and Schulze, <i>ibid.</i> 1897, 30, 53, Vorontsov, Amer. Chem. Abstr. 1940, 2360) or of $\beta$ -naphthylamine-5-sulphonic acid (Witt, Ber. 1888, 21, 3486).	<i>Acid</i> , HA, sparingly soluble leaflets. Is decomposed by nitrous acid and does not couple with diazotised bases.
1:2:6	Reduction of azo derivatives of $\beta$ -naphthylamine-6-sulphonic acid (Witt, <i>ibid.</i> 1888, 21, 3484).	<i>Acid</i> , sparingly soluble needles; <i>sodium</i> salt, scales. Is decomposed by nitrous acid and does not couple with diazotised bases.
1:2:7	Reduction of azo derivatives of $\beta$ -naphthylamine-7-sulphonic acid (Witt, <i>ibid.</i> 1888, 21, 3485).	<i>Acid</i> , grey powder. Is decomposed by nitrous acid and does not couple with diazotised bases.
1:3:5	$\alpha$ -Naphthol-3:5-disulphonic acid heated with ammonia under pressure at 175° (Kalle, G.P. 94075).	<i>Acid</i> , readily soluble. Couples with diazotised bases. For <i>diaryl</i> derivatives, <i>cf.</i> Bayer, G.P. 77866; 78854; B.P. 16780; 19623, 1893.
1:3:6	$\alpha$ -Naphthylamine- or $\alpha$ -naphthol-3:6-disulphonic acid heated with ammonia under pressure at 160–180° (Kalle, G.P. 89061; 94075; B.P. 9103, 1895; Friedländer and Taussig, Ber. 1897, 30, 1462).	<i>Acid</i> , sparingly, <i>sodium</i> salt readily, soluble. Forms yellow <i>diazo</i> -compound. Couples with diazotised bases. For <i>diaryl</i> derivatives, <i>cf.</i> Bayer, G.P. 76414; 77866; 78854; B.P. 8898; 16780; 19623, 1893).
1:3:7	$\alpha$ -Naphthylamine- or $\alpha$ -naphthol-3:7-disulphonic acid heated with ammonia under pressure at 160–180° (Kalle, G.P. 89061; B.P. 9103, 1895).	<i>Acid</i> , very sparingly soluble needles. Gives reddish-brown coloration with ferric chloride. For <i>diaryl</i> derivatives, <i>cf.</i> Bayer, <i>l.c.</i>
1:3:8	$\alpha$ -Naphthylamine- or $\alpha$ -naphthol-3:8-disulphonic acid heated with ammonia under pressure at 160–180° (Kalle, G.P. 89061; B.P. 9103, 1895).	<i>Acid</i> , very sparingly soluble. Gives reddish-brown coloration with ferric chloride. For <i>diaryl</i> derivatives, <i>cf.</i> Bayer, <i>l.c.</i>

## DIAMINONAPHTHALENEMONOSULPHONIC ACIDS—continued.

Constitution.	Preparation.	Acids, salts, and reactions.
N:N:S 1:4:2	(1) Reduction of azo derivatives of $\alpha$ -naphthylamine-2-sulphonic acid (Levinstein, G.P.a. 5939; B.P. 2946, 1896; Oesterreich, cf. J.S.C.I. 1898, 17, 836). (2) Action of sodium bisulphite on [ $\alpha$ ]naphthaquinonechlorimide (Friedländer and Reinhardt, Ber. 1894, 27, 239).	<i>Acid</i> , very sparingly soluble. Gives dark green coloration with ferric chloride. In acetic acid solution forms <i>diazo</i> -compound with nitrous acid (1 mol.), convertible into $\alpha$ -naphthylamine-3-sulphonic acid and by coupling into azo-dyes in which the second amino-group can be diazotised and coupled to furnish <i>disazo</i> -dyes (Levinstein, l.c.; G.P. 102160).
1:4:5	Reduction of 4-nitro- $\alpha$ -naphthylamine-5-sulphonic acid (Bayer, G.P. 133951; Levinstein, B.P. 13178, 1899).	<i>Acid</i> , greyish needles, rapidly oxidised in alkaline solution.
1:4:6	(1) Sulphonation of acetyl-1:4-diaminonaphthalene with 20% anhydro-acid at 25–50° and subsequent deacetylation (Dahl, G.P. 66354; Ammelburg, J. pr. Chem. 1893, [II], 48, 286). (2) Reduction of azo derivatives of $\alpha$ -naphthylamine-6- or 7-sulphonic acid (Levinstein, B.P. 12119, 1898; Cassella, G.P. 116922). (3) As the mixed 1- and 4-acetyl derivatives by nitrating a mixture of acetylated $\alpha$ -naphthylamine-6- and 7-sulphonic acids and after salting out reducing the product (Cassella, G.P. 74177; B.P. 15444, 1893).	<i>Acid</i> , very sparingly soluble. With nitrous acid or ferric chloride forms [ $\alpha$ ]naphthaquinone (Dahl, l.c.). <i>Formyl</i> derivative (Gaess, G.P. 138030; 138031; B.P. 3162; 8195, 1902). <i>Acetyl</i> derivative (Dahl, l.c.; cf. Bayer, G.P. 109609); <i>acid</i> , HA, needles, and <i>lead</i> salt, $PbA_2 + 1\frac{1}{2}H_2O$ , very sparingly, but <i>zinc</i> , $ZnA_2 + 3\frac{1}{2}H_2O$ , needles, <i>barium</i> , $BaA_2 + 7H_2O$ , flat prisms, and <i>potassium</i> salt, KA, needles, easily soluble (Ammelburg, l.c.). Gives brilliant blue coloration with ferric chloride and is diazotised by nitrous acid.
1:5:2	(1) Reduction of 5-nitro- $\alpha$ -naphthylamine-2-sulphonic acid (Cassella, G.P. 70890; Friedländer and Kielbasinski, Ber. 1896, 29, 1983). (2) Sulphonation of 1:5-diaminonaphthalene sulphate with 5% anhydro-acid at 100° (Bucherer and Uhlmann, J. pr. Chem. 1909, [II], 80, 213).	<i>Acid</i> , sparingly soluble small needles; <i>sodium</i> salt readily; <i>barium</i> salt, $BaA_2$ , sparingly soluble. Forms an easily soluble yellow <i>tetrazo</i> -compound. Couples with 1 mol. or 2 mol. of a diazotised base.
1:5:3	Nitration and reduction of $\alpha$ -nitronaphthalene-7-sulphonic acid (Cassella, G.P. 85058), or, mixed with 1:8:3-acid, of naphthalene- $\beta$ -sulphonic acid (Cassella, G.P. 67017; B.P. 6972, 1891).	<i>Acid</i> , sparingly, salts readily soluble; <i>hydrochloride</i> , prisms. Forms a <i>tetrazo</i> -compound.
1:5:4	(1) Reduction and deacetylation of 5-nitroacetyl- $\alpha$ -naphthalide-4-sulphonic acid (Nietzki and Zübelen, Ber. 1889, 22, 451; Bucherer and Uhlmann, J. pr. Chem. 1909, [II], 80, 255). (2) From 1:5-dihydroxynaphthalene-4-sulphonic acid heated with ammonium bisulphite solution and ammonia (Bucherer and Uhlmann, l.c.).	<i>Acid</i> , very sparingly soluble. Forms a <i>tetrazo</i> -compound. Couples with diazotised bases.
1:6:4	1-Amino-6-naphthol-4-sulphonic acid heated with ammonia under pressure at 170–180° (Dahl, G.P. 65834; 71157; B.P. 4110, 1892; Friedländer and Kielbasinski, Ber. 1896, 29, 1979).	<i>Acid</i> , very sparingly soluble needles; <i>barium</i> and <i>sodium</i> , $NaA + 1\frac{1}{2}H_2O$ , salts flat prisms moderately soluble. Forms a <i>tetrazo</i> -compound which decomposes at 0° into a <i>diazonaphtholsulphonic acid</i> . Couples with diazotised bases.
1:8:3	Nitration and reduction of $\alpha$ -nitronaphthalene-6-sulphonic acid (Cassella, G.P. 85058), or, mixed with 1:5:3-acid, of naphthalene- $\beta$ -sulphonic acid (Cassella, G.P. 67017; B.P. 6972, 1891).	<i>Acid</i> , sparingly soluble needles; <i>alkali</i> salts readily soluble; <i>hydrochloride</i> needles. Forms an <i>azimino</i> derivative. Couples with 1 mol. or 2 mol. of diazotised bases.
1:8:4	(1) Reduction of 1:8-dinitronaphthalene-4-sulphonic acid (Cassella, G.P. 70019; B.P. 4613, 1893). (2) Acid sulphate of 1:8-diaminonaphthalene "baked" above 100° in a vacuum (Bayer, G.P. 216075; B.P. 6831, 1909).	<i>Acid</i> , almost insoluble; <i>sodium</i> salt readily soluble; <i>hydrochloride</i> and <i>sulphate</i> crystallise well. Forms an <i>azimino</i> derivative (cf. Cassella, G.P. 77425; B.P. 24714, 1893). Couples with 1 mol. or 2 mol. of diazotised bases.
2:3:6	2:3-Dihydroxynaphthalene-6-sulphonic acid or 2-amino-3-naphthol-6-sulphonic acid, heated with ammonia under pressure at 150–220° (Atklenges., G.P.a. 3676; B.P. 8381, 1894; Oesterreich, cf. J.S.C.I. 1898, 17, 836).	<i>Acid</i> , sparingly soluble; <i>sodium</i> salt leaflets, showing blue fluorescence in solution; <i>barium</i> salt, $BaA_2$ . Gives brown coloration with ferric chloride. Forms an <i>azimino</i> derivative. Couples with 1 mol. of diazotised bases (Oesterreich, l.c.) but with 2 mol. of diazotised <i>p</i> -nitraniline (Atklenges., G.P. 84461).
2:6:4	Reduction of 6-nitro- $\beta$ -naphthylamine-8-sulphonic acid (Friedländer and Lucht, Ber. 1893, 26, 3033).	<i>Acid</i> , sparingly soluble flat prisms. Gives emerald-green coloration with ferric chloride (Jacchia, Annalen, 1902, 323, 130).

## DIAMINONAPHTHALENEDISULPHONIC ACIDS.

Constitution.	Preparation.	Acids, salts, and reactions.
N:N:5:5 1:2:3:6	Reduction of azo derivatives of $\alpha$ -naphthylamine-3:6-disulphonic acid (Witt, Ber. 1888, 21, 3487).	<i>Acid</i> , sparingly soluble; <i>acid sodium salt</i> , NaHA, needles. Gives emerald-green coloration with ferric chloride. Decomposed by nitrous acid. Does not couple in acid solution (Cassella, G.P. 72584).
1:2:3:8	Reduction of azo derivatives of $\alpha$ -naphthylamine-3:8-disulphonic acid (Berntsen, <i>ibid.</i> 1890, 23, 3094).	<i>Acid sodium salt</i> , $\text{NaH}_2\text{A} + 3\text{H}_2\text{O}$ , needles. <i>Anhydride</i> (sultam), $\text{C}_{10}\text{H}_8\text{O}_5\text{N}_2\text{S}_2 + 2\text{H}_2\text{O}$ , sparingly soluble long needles.
1:3(5):7	$\alpha$ -Naphthol-3:5:7-trisulphonic acid heated with ammonia and ammonium chloride under pressure at 160–180° (Kalle, G.P. 90906; B.P. 9103, 1895).	<i>Acid</i> , very sparingly soluble needles. Gives yellowish-red coloration with ferric chloride, and brown with nitrous acid. Couples with diazotised bases.
1:3:6:8	$\alpha$ -Naphthol- or $\alpha$ -naphthylamine-3:6:8-trisulphonic acid heated with ammonia and ammonium chloride at 160–180° (Kalle, G.P. 90905; B.P. 9103, 1895).	<i>Acid</i> , sparingly soluble leaflets. Gives intense green coloration with ferric chloride and brown with nitrous acid. Couples with diazotised bases. For <i>diaryl</i> derivatives, cf. Bayer, G.P. 77866; 78854; B.P. 16780; 19623, 1893.
1:5:3:7	Reduction of 1:5-dinitronaphthalene-3:7-disulphonic acid (Cassella, G.P. 61174; B.P. 15346, 1890 cf. Oehler, G.P.a. 1430; Bayer, G.P. 126198).	<i>Acid</i> , very sparingly soluble leaflets; <i>sodium</i> and <i>barium</i> salts sparingly soluble. Forms an insoluble <i>tetrazo</i> -compound (cf. Cassella, G.P. 62075; B.P. 15346, 1890). Couples with diazotised bases.
1:5:4:(8)	1:5-Dinitronaphthalene heated with sodium bisulphite solution in a reflux apparatus or under pressure (Fischesser, G.P. 79577; B.P. 13156, 1894).	<i>Acid</i> , readily soluble; <i>acid barium salt</i> , $\text{Ba}(\text{HA})_2 + 10\text{H}_2\text{O}$ , moderately soluble. Gives a reddish-blue coloration with ferric chloride. Forms a <i>tetrazo</i> -compound, and couples.
1:6:3:8	Reduction of 1:6-dinitronaphthalene-3:8-disulphonic acid (Friedländer and Kielbasinski, Ber. 1896, 29, 1982; cf. <i>ibid.</i> , p. 2574).	<i>Acid</i> , sparingly soluble; <i>sodium salt</i> , $\text{Na}_2\text{A}$ , easily soluble needles, showing violet fluorescence in solution. Couples with diazotised bases.
1:6:4:8	Reduction of 1:6-dinitronaphthalene-4:8-disulphonic acid (Kalle, G.P. 72665; Friedländer and Kielbasinski, <i>ibid.</i> 1896, 29, 1980; cf. <i>ibid.</i> , p. 2574).	<i>Acid</i> , sparingly soluble. Gives cherry-red coloration with ferric chloride. Forms a sparingly soluble <i>tetrazo</i> -compound. Couples with diazotised bases.
1:8:(2):5	1:8-Diaminonaphthalene-4-sulphonic acid sulphonated with 8% anhydro-acid at 80° (Cassella, G.P. 72584).	<i>Acid</i> and <i>sodium salt</i> readily soluble. Forms an <i>azimino</i> derivative. Couples readily with 1 mol., less readily with 2 mol., of diazotised bases.
1:8:3:6	Reduction of 1:8-dinitronaphthalene-3:6-disulphonic acid (Cassella, G.P. 67062; B.P. 1742, 1891; Bayer, G.P. 69190; B.P. 11522, 1892).	<i>Acid potassium salt</i> , $\text{KHA} + 3\text{H}_2\text{O}$ , needles, <i>acid barium salt</i> , $\text{Ba}(\text{HA})_2 + 6\text{H}_2\text{O}$ , sparingly soluble needles. Gives reddish-brown coloration with ferric chloride. Forms an <i>azimino</i> derivative (Cassella, G.P. 69963). Couples with diazotised bases.
2:3:6:8	2-Amino-3-naphthol-6:8-disulphonic acid heated with 30% ammonia under pressure at 185–190° (Aktienges., G.P. 86448; B.P. 8645, 1895).	<i>Acid</i> , sparingly soluble needles, <i>sodium salt</i> , readily soluble.
2:6:?:?:	2:6-Dihydroxynaphthalenedisulphonic acid heated with ammonia and ammonium chloride under pressure at 200° (Jacchia, Annalen, 1902, 323, 131).	<i>Acid</i> , $\text{H}_2\text{A} + 4\frac{1}{2}\text{H}_2\text{O}$ , leaflets.
2:7:3:6	2:7-Dihydroxynaphthalene-3:6-disulphonic acid heated with ammonia under pressure at 200–220° (Aktienges., G.P.a. 3686; B.P. 3844, 1894).	<i>Acid</i> , sparingly, <i>sodium salt</i> , readily soluble. Gives faint brown coloration with ferric chloride. Forms a sparingly soluble <i>tetrazo</i> -compound. Couples with diazotised bases.

1:8-Diaminonaphthalene-2:4:5-trisulphonic Acid is obtained when 1:8-dinitronaphthalene is heated with sodium bisulphite solution (Fischesser & Co.; G.P. 79577; B.P. 13156, 1894; Bucherer and Barsch, J. pr. Chem. 1925, [ii], 111, 313). The *acid sodium salt*,  $\text{Na}_2\text{HA} + 2\text{H}_2\text{O}$ , is readily soluble, but the *acid barium salt*,  $\text{BaHA} + 2\text{H}_2\text{O}$ , only sparingly soluble. The coloration with ferric chloride is yellowish-brown. It forms an *azimino* derivative, and couples with 1 mol. of diazotised base.



## TRIAMINONAPHTHALENES.

(i) 1:2:6-Triaminonaphthalene, obtained by reduction of 1:6-dinitro- $\beta$ -naphthylamine (cf. Kehrman and Matis, Ber. 1898, 31, 2419), forms a *triacetyl* derivative, needles, m.p. 280°, and gives the reactions of an *o*-diamine (Loewe, *ibid.* 1890, 23, 2544).

(ii) 1:3:6-Triaminonaphthalene, obtained by heating 1:6-dihydroxynaphthalene-3-sulphonic acid with ammonia and ammonium chloride under pressure at 160–180°, is easily, but its *sulphate* only sparingly soluble. Its solution is coloured deep brown by nitrous acid (Kalle, G.P. 89061; B.P. 9103, 1895).

(iii) 1:3:7-Triaminonaphthalene, obtained by heating 1:7-dihydroxynaphthalene-3-sulphonic acid or 2-amino-6-naphthol-8-sulphonic acid with ammonia and ammonium chloride at 160–180°, is easily soluble and in solution gives a deep brown coloration with nitrous acid, but bluish-violet with ferric chloride. The *sulphate* is only sparingly soluble (Kallo, G.P. 90905; B.P. 9103, 1895).

(iv) and (v) 1:2:5- and 1:4:8-Triaminonaphthalenes, have been obtained from the 1:5- and 1:8-diamines by coupling with diazotoluene and reducing the respective dyes (Finzi, J.C.S. 1925, 128, i, 701).

(vi) 1:3:4-Triaminonaphthalene forms a *triacetyl* derivative, m.p. 301° (Panizzon-Favre, Gazzetta, 1924, 54, 826).

## NAPHTHOLS.

The common general method of preparation of the naphthols and naphtholsulphonic acids, on the large scale, is by fusion of the appropriate naphthalenesulphonic acid with caustic alkali. Other methods are from the corresponding naphthylamines, by hydrolysis with dilute acid at high temperatures, by the bisulphite reaction (see p. 273c), or through the diazo-compound.

Hydroxynaphthalenes resemble the hydroxy-benzenes in chemical behaviour but the hydroxyl group is more reactive. Thus, the naphthols are readily converted into naphthylamines by heating with ammonia under pressure (Badische, G.P. 14612; B.P. 2516, 1880), into alkyl ethers by heating with alcohol and sulphuric acid (Gattermann, Annalen, 1888, 244, 72), and into naphthyl ethers by boiling with dilute sulphuric acid (Graebe, Ber. 1880, 13, 1850). This reactivity is reduced, and the resemblance become more complete, on hydrogenation of the non-substituted ring (Bamberger, Annalen, 1890, 257, 10; see *ar*-tetrahydronaphthols, p. 422b).

 $\alpha$ -Naphthol.

$\alpha$ -Naphthol, or 1-hydroxynaphthalene, occurs in very small amount in coal-tar fractions of high boiling-point (Schulze, *ibid.* 1885, 227, 150). It may be prepared from  $\alpha$ -chloronaphthalene by digestion with aqueous (10%) caustic soda at temperatures up to 400° in the absence of catalysts (in the presence of active-copper catalysts mixed naphthols are obtained) (Dow Chem. Co., U.S.P. 1996744; Meyer and Bergius, Ber. 1914, 47, 3159); or, in better yield, by digestion with caustic soda and methyl alcohol at 210° (Chem. Werke. Ichendorf, G.P. 281175); or from  $\alpha$ -bromonaphthalene in 90–92% yield

by heating with aqueous caustic soda at 180–250° under pressure with a copper catalyst.

**Preparation.**—It is manufactured from  $\alpha$ -naphthylamine by heating with diluted sulphuric acid to 200° under pressure in a lead-lined autoclave, yield 94–95% theory (Höchst, G.P. 74879; B.P. 14301, 1892; Voroschov and Gutorko, J. Gen. Chem. Russ. 1935, 5, 1518; A. 1936, 720), or from naphthalene- $\alpha$ -sulphonic acid by fusion with caustic soda at 275–310° (Levinstein, B.P. 2300, 1883; Nat. Aniline and Chem. Co. Inc. U.S.P. 1949243; 1962137; 2025197). The former method gives a product entirely free from  $\beta$ -naphthol.

**Properties.**— $\alpha$ -Naphthol crystallises in lustrous, monoclinic flat prisms (cf. Steinmetz, Z. Kryst. Min. 1916, 55, 373), m.p. 95.8–96.0°; b.p. 288.01°/760 mm. (Berliner, May and Linch, J. Amer. Chem. Soc. 1927, 49, 1012),  $d_4$  1.224 (Sehröder, Ber. 1879, 12, 1613). It is very sparingly soluble in hot water. It dissolves readily in organic solvents and in aqueous caustic alkali solutions. It has a phenolic odour and is readily volatile in steam. The sodium salt, scales, has m.p. 44–45° (Meldrum and Patel, J. Indian Chem. Soc. 1928, 5, 91; König, G.P. 216596).

**Reactions.**— $\alpha$ -Naphthol couples with diazotised bases forming *para*-azo-dyes. In alcoholic solution, with benzenediazonium chloride, it is said to give a mixture of the *ortho*- and *para*-compounds, of which the former is insoluble in 4% caustic soda solution (Charrier and Casale, Atti. R. Accad. Sei. Torino, 1914, 49, 477). With nitrous acid in aqueous solution it gives a mixture of chiefly 2- with some 4-nitroso- $\alpha$ -naphthol (see Naphthaquinoneoximes, p. 385a); in ethereal solution the product is the same as that obtained on nitration, 2:4-dinitro- $\alpha$ -naphthol. Chlorination with sulphuryl chloride gives 4-chloro- $\alpha$ -naphthol, with chlorine 2:4-dichloro- $\alpha$ -naphthol. On sulphonation,  $\alpha$ -naphthol-mono-, di-, and tri-sulphonic acids are obtained.

Oxidised with nitric acid, or with permanganate in acid solution, it gives *phthalic acid*; with permanganate in alkaline solution *phthalonic acid* (Henriques, Ber. 1888, 21, 1608); with aqueous ferric chloride at 70–80° a mixture of 4:4'-dihydroxy-1:1'-dinaphthyl and 1:1'-dihydroxy-2:2'-dinaphthyl (Joffe and Kristchevov, J. Gen. Chem. Russ., 1939, 9, 1136; A. 1939, II, 544); with peracetic acid in acetic acid below 40° *o*-carboxyalloccinnamic acid, [ $\alpha$ ]-naphthaquinone and a hydroxyquinone (Böeseken and von Königsfeldt, Rec. trav. chim. 1935, 54, 313). It is deoxygenated by the action of hydrogen under high pressure at elevated temperature in presence of ammonium molybdate and sulphur giving naphthalene, etc. (Hall, Fuel, 1933, 12, 419). Heated under pressure with ammonia, acetamide, or aniline,  $\alpha$ -naphthylamine, or its *acetyl* or *phenyl* derivative respectively, is obtained. The dried sodium derivative, heated with carbon dioxide under pressure, yields 1-hydroxy-2-naphthoic acid.  $\alpha$ -Naphthol heated in alcoholic solution with carbon tetrachloride, acid binders, and a suitable catalyst, gives  $\alpha$ -naphthol-2:4-dicarboxylic acid (Soc. Chem. Ind. in Basle, G.P. 373737). The condensation product with dimethylolcarbamide gives, on



hydrolysis with boiling hydrochloric acid,  $\alpha$ -di(1-hydroxy-2-naphthyl) ethane (De Diesbach, Wanger, and Stockalper, *Helv. Chim. Acta*, 1931, 14, 355). Boiled in air, or distilled with litharge, it gives  $\alpha$ -dinaphthylene oxide (Graebe, *et al.*, *Annalen*, 1881, 209, 134).

$\alpha$ -Naphthol gives molecular compounds having fungicidal properties with 1-chloro-2:4-dinitrobenzene, yellow needles, m.p. 105°; trinitrobenzene, orange crystals, m.p. 198°; 2:4-dinitrotoluene, yellow crystals, m.p. 98° (Buehler, Hisey, and Wood, *J. Amer. Chem. Soc.* 1930, 52, 1939; I.G., G.P. 462151; Hertel, *Annalen*, 1927, 451, 179).

**Colour Reactions.**—In aqueous solution hypochlorite gives first a dark violet solution and then a flocculent precipitate (*see* Ekkert, *Pharm. Zentr.* 1930, 71, 433); ferric chloride gives a milky opalescence changing to a violet flocculent precipitate of the dinaphthol. Like  $\beta$ -naphthol it develops a Prussian-blue coloration with chloroform and caustic potash solution, but, unlike  $\beta$ -naphthol, it gives a deep violet turbid liquid when mixed in aqueous solution with sodium hypoiodite, and an intense green coloration, changing to reddish-violet on addition of acetic acid, when shaken in small amount (0.01–0.02 g.) with 2–3 c.c. of titanyl sulphate solution (Deniges, *Ann. Chim. Analyt.*, 1916, 21, 216).

**Tests.**—Commercial  $\alpha$ -naphthol is a light grey crystalline powder, crystallising point above 91.5°, containing not more than 0.1% of material insoluble in aqueous caustic soda. It may be distinguished from  $\beta$ -naphthol by the violet coloration which it gives on addition of a trace of copper salt to a neutral or faintly acid solution (Aloy and Valdiguié, *Bull. Soc. chim.* 1922, [iv], 31, 1176). For other tests, qualitative and quantitative, *see* Callan, *J.S.C.I.* 1925, 44, 125r.

$\beta$ -Naphthol to the extent of 15–20% may be removed from crude  $\alpha$ -naphthol as an insoluble calcium compound (Penn. Coal Prod. Co., U.S.P. 1717009).

**Estimation.**—The *picrate*, m.p. 189–190°, almost insoluble in water, may be employed (Küster, *Ber.* 1894, 27, 1104).

$\alpha$ -Naphthyl Methyl Ether is prepared by heating  $\alpha$ -naphthol (5 parts) with absolute methyl alcohol (5 parts) and sulphuric acid (2 parts) at 140° under reflux (Gattermann, *Annalen*, 1888, 244, 72). It is an oil with an orange-like odour, volatile in steam, b.p. 269°,  $\rho$  15° 1.0974. It forms equimolecular double compounds with dinitro-compounds such as *m*-dinitrobenzene (*see* A. 1939, II, 544).

$\alpha$ -Naphthyl Ethyl Ether is prepared in the same way as the methyl ether (Gattermann, *l.c.*). It has a peculiar odour, m.p. 5.5°, b.p. 276°, and is volatile in steam. Condensed with formaldehyde, in presence of acidic catalyst, it gives a resinous material (Höchst, G.P. 403645).

**Reactions.**—Like other  $\alpha$ -naphthyl ethers, it couples with diazotised bases containing *p*- or *o*-*p*-negative radicals, *e.g.*, diazotised 2:4-dinitroaniline, forming azo-dyes (Meyer, Irschick, and Schlösser, *Ber.* 1914, 47, 1750). On sulphonation it yields 1-ethoxynaphthalene-4-sulphonic acid from which, by nitration, 2:4-dinitro- $\alpha$ -naphthol, 4-nitro- $\alpha$ -naphthyl ethyl ether, and 2-nitro-1-ethoxynaphthalene-4-sulphonic acid

are formed (Witt and Schneider, *ibid.* 1901, 34, 3173).

$\alpha$ -Naphthyl Phenyl Ether, m.p. 55–56°, is obtained by heating a solution of sodium  $\alpha$ -naphthoxide in  $\alpha$ -naphthol with chlorobenzene at 200–220° under pressure (Fritzsche, *B.P.* 9797, 1913).

Other ethers, including  $\alpha$ -naphthyl  $\beta$ -hydroxyethyl ether are described by Kirner and Richter, *J. Amer. Chem. Soc.* 1929, 51, 3409. Naphthyl ethers may be identified as picrates (Dermer and Dermer, *J. Org. Chem.* 1938, 3, 289).

$\alpha\alpha'$ -Dinaphthyl Carbonate, prepared by the interaction of phosgene and sodium  $\alpha$ -naphthoxide, is a crystalline powder, m.p. 129–130°, convertible into  $\alpha$ -naphthol-4-sulphonic acid or a mixture of  $\alpha$ -naphthol-4:6- and -4:7-disulphonic acids by sulphonation (Reverdin, *Ber.* 1894, 27, 3459; Höchst, *B.P.* 14134–5, 1894).

$\alpha\alpha'$ -Dinaphthyl Sulphite, m.p. 92–93°, is obtained by heating  $\alpha$ -naphthol in carbon disulphide solution with thionyl chloride in the presence of pyridine (Badische, G.P. 303033).

$\alpha$ -Naphthyl Acetate, prepared by heating  $\alpha$ -naphthol with acetic acid at 200° (Graebe, *Annalen*, 1881, 209, 151), broad needles or tables, m.p. 49°, is hydrolysed by boiling water, gives [ $\alpha$ ]naphthaquinone on oxidation with chromic acid in acetic acid solution, and a mixture of 1-hydroxy-4- and -2-naphthyl methyl ketones when treated with aluminium chloride (Lederer, *J. pr. Chem.* 1932, [ii], 135, 19).

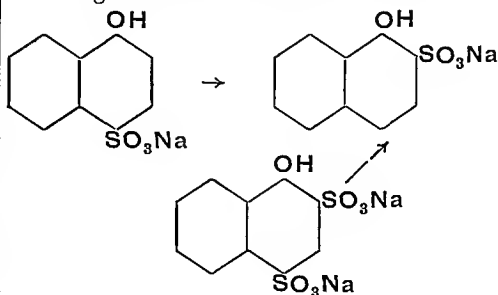
#### $\alpha$ -NAPHTHOLSULPHONIC ACIDS.

The general methods of preparation are:

1. Sulphonation of  $\alpha$ -naphthol;
2. Exchange of the amino-group in  $\alpha$ -naphthylaminesulphonic acids for hydroxyl by the diazo-reaction, or by the bisulphite reaction, or by interaction with water at a high temperature;
3. Exchange of chlorine in  $\alpha$ -chloronaphthalenesulphonic acids for hydroxyl by fusion with caustic alkali;
4. Exchange of one sulphonic group in naphthalenepolysulphonic acids for hydroxyl by fusion with caustic alkali.

Other methods of less importance, or more limited application, are:

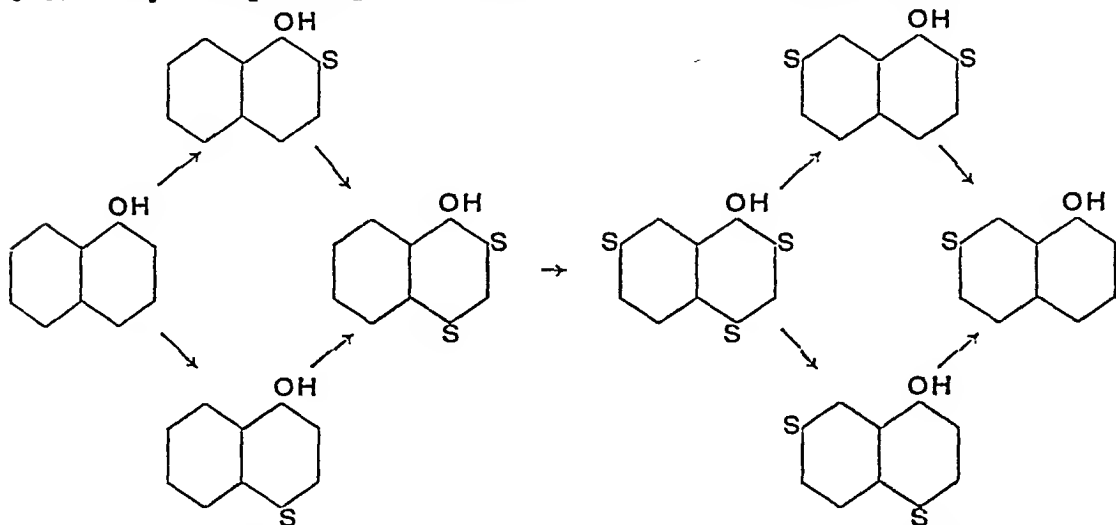
- (a) Partial hydrolysis of  $\alpha$ -naphtholpolysulphonic acids by interaction, either with dilute acids at a high temperature, or with sodium amalgam in the cold;
- (b) The change which sodium  $\alpha$ -naphthol-4-sulphonate and -2:4-disulphonate undergo when heated at 170°:



The  $\alpha$ -naphtholsulphonic acids and their salts are more soluble than the  $\alpha$ -naphthylaminesulphonic acids. They are less easy to recognise in, or to isolate from, mixtures containing them than the former. The acids have been identified by their salts (e.g., zinc salts) or through the *o*-carbethoxy- $\alpha$ -naphtholsulphonyl chlorides

(Gebauer-Fülneegg and Glückmann, *Monatsh.*, 1929, 53-54, 100), by means of nitrous acid (forming *o*- or *p*-nitroso derivatives), nitric acid (producing Naphthol Yellows), or by coupling with various diazonium compounds.

The products of the action of sulphuric acid on  $\alpha$ -naphthol are as follows:



The last three acids are formed by partial hydrolysis of the trisulphonic acid by relatively dilute acid at the highest temperature employed in the sulphonations. The 3-, 5-, and 8-positions are not filled by direct action of sulphuric acid on  $\alpha$ -naphthol or any  $\alpha$ -naphtholsulphonic acids. The same is true of the action of chlorosulphonic acid (Pollak, Gebauer-Fülneegg and Blumenstock-Halward, *ibid.* 1928, 49, 187; *ibid.* 1929, 53-54, 100; Gebauer-Fülneegg and Haemmerle, *J. Amer. Chem. Soc.* 1931, 53, 2648; cf. Kalle, G.P. 343056).

$\alpha$ -Naphtholsulphonic acids, with a sulphonic group in the 3-position, by interaction with ammonia, give 1:3-diaminonaphthalene derivatives; those with the sulphonic group in the 3-, 4-, or 5-position couple to give *ortho*-azo dyes; those with the sulphonic group in the 8-position give *peri*-anhydrides.

#### $\alpha$ -NAPHTHOLMONOSULPHONIC ACIDS.

In every case where the constitution of an  $\alpha$ -naphtholsulphonic acid is given, the hydroxyl radical is supposed to be in position "1." The technically important  $\alpha$ -naphtholmonosulphonic acids are the 4- and 5-isomers.

(i)  $\alpha$ -Naphthol-2-sulphonic Acid is never a sole product of sulphonation of  $\alpha$ -naphthol, much 4-mono- and 2:4-disulphonic acids being present (Conrad and Fischer, *Annalen*, 1893, 273, 109; Bender, *Ber.* 1889, 22, 999). If  $\alpha$ -naphthol is heated only for a short time with an equal weight of sulphuric acid at 60-70°, so that sulphonation is incomplete, a yield of 50% is obtained; the acid can be separated as potassium salt by addition of potassium chloride to the sulphonation mass slightly diluted with water (Friedländer and Taussig, *ibid.* 1897, 30, 1457). Holdemann tried mercurous sulphate as a catalyst in the reaction without effect on the proportion of 2-sulphonic acid formed (*ibid.* 1906, 39, 1255).

Pollak, Gebauer-Fülneegg and Blumenstock-Halward (*l.c.*) report that the 2-sulphonic acid is produced by the action of 2 parts of chlorosulphonic acid on 1 part of  $\alpha$ -naphthol in the cold.

**Preparation.**—It may be prepared either from  $\alpha$ -naphthol by Friedländer and Taussig's method (*l.c.*), or from  $\alpha$ -naphthylamine-2-sulphonic acid by the diazo-reaction (Cleve, *ibid.* 1891, 24, 3476); or its sodium salt may be obtained in 70-80% yield by heating sodium  $\alpha$ -naphthol-4-sulphonate or -2:4-disulphonate, mixed with twice its weight of naphthalene or paraffin, during 3-4 hours at 160-170° (Bayer, G.P. 237396; B.P. 2355, 1911).

**Salts.**—The acid forms small rhombic prisms, and differs from its isomers in being sparingly soluble in dilute mineral acids. The lead salt,  $PbA_2 + H_2O$ , scales; barium salt,  $BaA_2 + 1\frac{1}{2}H_2O$ , needles; and calcium salt,  $CaA_2 + H_2O$  (?), scales, are sparingly soluble (Cleve, *l.c.*); the potassium salt,  $KA + \frac{1}{2}H_2O$ , prisms, is soluble in 37 parts of water at 18°, but almost insoluble in saturated potassium chloride solution (Conrad and Fischer, *l.c.*).

**Reactions.**—With nitrous acid in the cold it forms 4-nitroso- $\alpha$ -naphthol-2-sulphonic acid, which does not give a Naphthol Green with iron salts. With nitric acid it yields 2:4-dinitro- $\alpha$ -naphthol. On sulphonation it gives, first  $\alpha$ -naphthol-2:4-disulphonic acid, thereafter as shown in the diagram above.

The acetyl derivative is convertible into the sulphonyl chloride, m.p. 87.5° (Anschütz and Maxim, *Annalen*, 1918, 415, 92; Gesellsch., B.P. 232620).

(ii)  $\alpha$ -Naphthol-3-sulphonic Acid is obtained by fusing naphthalene-1:3-disulphonic acid with caustic alkali at 200-220° (Badische, G.P. 57910; B.P. 9537, 1890); or by boiling diazotised  $\alpha$ -naphthylamine-3-sulphonic acid with 10% sulphuric acid (Gattermann and

Schulze, Ber. 1897, 30, 54), or diazotised 2-amino-8-naphthol-6-sulphonic acid with alcohol (Badische, l.c.; Friedländer and Taussig, *ibid.* 1897, 30, 1458); or by reduction of  $\alpha$ -naphthol-3:8-disulphonic acid with sodium amalgam, or electrolytically (Bayer, G.P. 255724; B.P. 28172-3, 1911; G.P. 248527; 251094).

**Salts.**—The zinc salt,  $\text{ZnA}_2 + 8\frac{1}{2}\text{H}_2\text{O}$ , forms long needles and, like the barium salt, is easily soluble in water (Friedländer and Taussig, l.c.).

**Reactions.**—With diazotised aniline, *o*-nitroaniline and *p*-nitroaniline, it couples respectively, in the *ortho*, in the *para*, or in both the *ortho* and the *para*-positions (Gattermann and Schulze, l.c.; Gattermann and Liebermann, Annalen, 1912, 393, 214). Heated with ammonia, under pressure, at 160–180° it gives 1:3-diaminonaphthalene, and with aniline and its hydrochloride, at 150–170°, 1:3-dianilinonaphthalene. By digestion with 60% caustic soda at 180° it gives *o*-toluic acid (Kalle, G.P. 79028; B.P. 16559, 1894).

(iii)  $\alpha$ -Naphthol-4-sulphonic Acid (Nevile and Winther's acid), is one of the products of sulphonation of  $\alpha$ -naphthol (for its isolation, see Friedländer and Taussig, Ber. 1897, 30, 1458). It was obtained by Nevile and Winther (J.C.S. 1880, 37, 632) by boiling the diazo-compound from  $\alpha$ -naphthylamine-4-sulphonic acid with 10% sulphuric acid.

**Preparation.**—By heating the sodium salt of  $\alpha$ -naphthylamine-4-sulphonic acid with 50% caustic soda solution under pressure at 240–260°, and boiling the solution of the product in water to expel ammonia (Aktienges., G.P. 46307); or pure, and in almost quantitative yield, from naphthionic acid by interaction with sodium bisulphite to give the sulphurous ester and hydrolysing the product (Bayer, G.P. 109102; B.P. 16807, 1899). For the latter purpose Du Pont (U.S.P. 1580714) use an alkaline earth, giving a sparingly soluble sulphite, which may be removed by filtration.

Alternative methods are to digest  $\alpha$ -chloronaphthalene-4-sulphonic acid with aqueous caustic soda under pressure at 200–220° (Oehler, G.P. 77446; see also Voroschov and Karlasch, Anilinokras. Prom. 1934, 4, 545; B. 1935, 137); to sulphonate  $\alpha$ -naphthyl carbonate with monohydrate at 10–20°, isolating the disulpho- $\alpha$ -naphthyl carbonate and heating the product with water at 60–70° (Reverdin, Ber. 1894, 27, 3460); or to sulphonate  $\alpha$ -naphthol in a solvent, such as tetrachloroethane, with chlorosulphonic acid, when not more than 1–2% of isomeric acids are formed (B.D.C., B.P. 186515).

**Salts.**—The acid and its salts are easily soluble. The zinc salt,  $\text{ZnA}_2 + 8\text{H}_2\text{O}$ , forms prisms, the sodium salt, easily salted from solutions, forms columnar crystals, is soluble in 90% alcohol and with ferric chloride solution gives a blue or bluish-green coloration. Numerous arylamine salts are described by Forster and Watson (J.S.C.I. 1927, 46, 224t), the aniline salt, m.p. 186–187°, being soluble to the extent of 5.38 parts/100 parts of 1% acetic acid at 15°. The amide melts at 223° (Gesellsch., B.P. 232620).

**Reactions.**—The *ortho*-azo-dyes, produced on coupling with diazotised bases, are of technical importance, e.g., Chlorazol Azurine G, Chlorazol

Violet R, Naphthalene Scarlet B, etc. Nitrou acid in the cold gives 2-nitroso- $\alpha$ -naphthol-4-sulphonic acid, which, with iron salts, gives a Naphthol Green. With warm dilute nitric acid it forms 2:4-dinitro- $\alpha$ -naphthol (Bender, Ber. 1889, 22, 997). The action of ammonium sulphite solution and ammonia at 100–150° furnishes  $\alpha$ -naphthylamine-4-sulphonic acid; with ethylenediamine and sodium bisulphite the sodium salt gives 1-aminoethylamino-naphthalene-4-sulphonic acid, a dyestuff intermediate (Bayer, B.P. 230457; U.S.P. 1543569). Sulphonation yields successively  $\alpha$ -naphthol-2:4-disulphonic acid and  $\alpha$ -naphthol-2:4:7-trisulphonic acid. Its sodium salt heated at 160–170° is transformed into sodium  $\alpha$ -naphthol-2-sulphonate.

(iv)  $\alpha$ -Naphthol-5-sulphonic Acid (Oxy-L-acid), is obtained by fusing sodium naphthalene-1:5-disulphonate with aqueous caustic soda at 160–190°, the sodium salt being isolated after acidification of the diluted melt with hydrochloric acid (Ewer and Pick, G.P. 41934); by the action of sodium bisulphite on  $\alpha$ -naphthylamine-5-sulphonic acid, followed by boiling with an alkaline earth hydroxide (Du Pont, U.S.P. 1580714); or when  $\alpha$ -chloronaphthalene-5-sulphonic acid is heated with 8% caustic soda solution under pressure at 240–250° (Oehler, G.P. 76446).

**Salts.**—The acid has been isolated as a semi-crystalline, deliquescent mass; the zinc salt,  $\text{ZnA}_2 + 8\frac{1}{2}\text{H}_2\text{O}$ , easily soluble long needles (Friedländer and Taussig, Ber. 1897, 30, 1460); the sodium salt, readily soluble in warm alcohol, gives a violet-red coloration with ferric chloride.

**Reactions.**—Diazotised bases couple with it, forming *ortho*-azo dyes (Gesellsch., G.P. 66838; Gattermann and Schulze, Ber. 1897, 30, 52); if the diazonium salt contains negative constituents, coupling takes place usually in the *para*-position (Gattermann and Liebermann, Annalen, 1912, 393, 211). It is used as end component in Monolite Bordeaux BL, Carmoisine L, and Solochrome Black F. Nitrous acid in the cold forms 2-nitroso- $\alpha$ -naphthol-5-sulphonic acid, highly crystalline, giving a Naphthol Green with iron salts. With 20% oleum below 100°,  $\alpha$ -naphthol-2:5-disulphonic acid is produced. Fused with caustic soda at 220–260° it yields 1:5-dihydroxynaphthalene; with sodamide, in naphthalene suspension at 230°, 1-amino-5-naphthol.

(v)  $\alpha$ -Naphthol-6-sulphonic Acid has been obtained from  $\alpha$ -naphthylamine-6-sulphonic acid by the bisulphite method (Bayer, G.P. 109102; B.P. 16807, 1899); or from sodium naphthalene-1:6-disulphonate by fusion with caustic soda. Little is known of this acid.

(vi)  $\alpha$ -Naphthol-7-sulphonic Acid is a product of the sulphonation of  $\alpha$ -naphthol with sulphuric acid at 130°. The pure acid is obtained from  $\alpha$ -naphthylamine-7-sulphonic acid by the bisulphite method (cf. Bucherer, J. pr. Chem. 1904, [ii], 70, 347); or from 7-sulpho-1-hydroxy-2-naphthoic acid by heating it with a small quantity of water at 120° (Friedländer and Taussig, Ber. 1897, 30, 1461).

**Salts.**—The acid, a crystalline mass, giving with ferric chloride a brownish-violet coloration,

is, like its salts, easily soluble. The zinc salt,  $\text{ZnA}_2 \cdot 8\text{H}_2\text{O}$ , forms radiate groups of needles; the barium salt, needles.

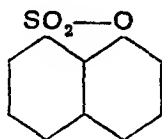
**Reactions.**—Coupled with diazotised *p*-nitro-aniline in acetic acid solution, it gives monoazo-dyes, but in alkaline solution, disazo-dyes sensitive to acids (Friedländer and Taussig, *l.c.*; cf. Bender, *ibid.* 1889, 22, 996). With nitrous acid it forms a *nitroso- $\alpha$ -naphthol-7-sulphonic acid*, which yields *2:4-dinitro- $\alpha$ -naphthol-7-sulphonic acid* on warming with dilute nitric acid.

(vii)  *$\alpha$ -Naphthol-8-sulphonic Acid* is obtained from  *$\alpha$ -naphthylamine-8-sulphonic acid*, either by action of water at  $180\text{--}220^\circ$  under pressure (Höchst, G.P. 74644; B.P. 14301, 1892), or by the bisulphite method. When diazotised  *$\alpha$ -naphthylamine-8-sulphonic acid* is boiled with water or dilute sulphuric acid, the product isolated is not the free acid but naphthasultone, the *peri*-anhydride, from which the acid is obtained, after hydrolysis with alcoholic ammonia at  $130^\circ$ , by decomposing the relatively insoluble lead salt with hydrogen sulphide. The sultone, with aqueous ammonia, in the cold, gives the acid *amide*, m.p.  $222^\circ$ , in 90% yield (Gesellsch., B.P. 207162; G.P. 407003).

**Salts.**—The acid,  $\text{HA} \cdot \text{H}_2\text{O}$ , is crystalline, m.p.  $106\text{--}107^\circ$ , and very soluble. It does not lose its water of crystallisation below  $180^\circ$ , and shows little tendency to pass into the anhydride (sultone), even in the presence of dehydrating agents. The *potassium* salt,  $\text{KA}$ , scales; the *basic sodium* salt,  $\text{Na}_2\text{A} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , small needles; and the *ammonium* salt,  $\text{NH}_4\text{A}$ , scales, are easily soluble in water, and, like the acid, give with ferric chloride a dark green coloration, changing rapidly to red.

**Reactions.**—It couples with diazotised bases. With nitrous acid a sparingly soluble *nitroso*-compound is obtained, which yields *2:4-dinitro- $\alpha$ -naphthol-8-sulphonic acid* when warmed with nitric acid. Fusion with caustic alkali gives *1:8-dihydroxynaphthalene*; with sodamido, in naphthalene suspension, *1-amino-8-naphthol*.

Naphthasultone,



is obtained almost quantitatively by boiling diazotised  *$\alpha$ -naphthylamine-8-sulphonic acid* in alcohol, water, or dilute sulphuric acid (Karpeles, J.S.C.I. 1898, 17, 837). It crystallises from alcohol in large prisms, m.p.  $154^\circ$ , distils above  $360^\circ$  with slight decomposition, and is almost insoluble in water.

**Reactions.**—It is hydrolysed by boiling dilute aqueous alkalis. With sulphuric acid it gives  *$\alpha$ -naphthol-4:8-disulphonic acid*. According to G.P. 430551 the *4-halogeno* derivative can be prepared from the sultone (at  $160\text{--}200^\circ$ ), from its 4-sulphonic acid or from  *$\alpha$ -naphthol-4:8-disulphonic acid* (at  $80^\circ$  in presence of hydrochloric acid) by action of halogen at a suitable temperature.  *$\alpha$ -Naphthol-6:8-disulphonic acid* under the same conditions gives, with chlorine, 4-

*chloronaphthasultone-6-sulphonic acid* (I.G., B.P. 433527). *4-Chloronaphthasultone* has m.p.  $176\text{--}178^\circ$ .

#### $\alpha$ -NAPHTHOLDISULPHONIC ACIDS.

(i)  *$\alpha$ -Naphthol-2:4-disulphonic Acid* is a product of direct sulphonation of  *$\alpha$ -naphthol* by about three times its weight of sulphuric acid at temperatures below  $100^\circ$  (Friedländer and Taussig, 1897, 30, 1457). It may be separated from mono- or other di-sulphonic acids present by removing these, either as sparingly soluble *nitroso*-compounds, formed by action of nitrous acid, or as insoluble azo-dyes, by suitable coupling (with diazotised xyldine). It may also be obtained from  *$\alpha$ -naphthol-2:4:8-trisulphonic acid* by reduction with sodium amalgam (Bayer, G.P. 255724; B.P. 28172, 1911). Its chloride (m.p.  $149^\circ$ ) is a product of the action of excess chlorosulphonic acid at ordinary temperature on  *$\alpha$ -naphthol* (Pollak, Gebauer-Fülneegg *et al.*, Monatsh. 1928, 49, 187).

**Identification.**—The *potassium* salt,  $\text{K}_2\text{A}$ , gives a deep blue coloration with ferric chloride. The acid is not precipitated either by lead or barium salts and yields neither azo-dyes nor a *nitroso*-compound (Conrad and Fischer, Annalen, 1893, 273, 105).

**Reactions.**—With nitric acid it gives *2:4-dinitro- $\alpha$ -naphthol*. On further sulphonation it gives  *$\alpha$ -naphthol-2:4:7-trisulphonic acid*.

(ii)  *$\alpha$ -Naphthol-2:5-disulphonic Acid* is prepared by sulphonation of  *$\alpha$ -naphthol-5-sulphonic acid*, with sulphuric acid or 20% oleum, below  $100^\circ$  (Bayer, G.P. 68344; B.P. 3397, 1890). The *sodium* salt, prisms, neither forms a *nitroso*-derivative nor couples with diazo-compounds (Gattermann and Schulze, Ber. 1897, 30, 55).

**Reaction.**—With 60% caustic soda solution at  $250^\circ$  it gives *1:5-dihydroxynaphthalene-2-sulphonic acid*.

(iii)  *$\alpha$ -Naphthol-2:7-disulphonic Acid* is one of the products of direct sulphonation of  *$\alpha$ -naphthol* with a relatively small proportion (2-3 parts) of sulphuric acid (approximately 93% strength) at  $125\text{--}130^\circ$  (cf. Friedländer and Taussig, *ibid.* 1897, 30, 1463; Leonhardt, B.P. 11318, 1887), but its isolation has not been described. It can be obtained from  *$\alpha$ -naphthylamine-2:7-disulphonic acid* by the diazo-reaction (Roverdin, and de la Harpe, Ber. 1892, 25, 1405) or from  *$\alpha$ -naphthol-2:4:7-trisulphonic acid* by reduction with sodium amalgam (Friedländer and Lucht, *ibid.* 1893, 26, 3031; Friedländer and Taussig, *l.c.*).

**Identification.**—The *zinc* salt,  $\text{ZnA}$ , is soluble. It couples *para*- with diazo-compounds. It gives a *nitroso* derivative, but this does not form a Naphthol Green with iron salts.

(iv)  *$\alpha$ -Naphthol-3:5-disulphonic Acid* has been obtained by fusing sodium naphthalene-1:3:5-trisulphonate with caustic soda at  $140\text{--}150^\circ$ , but is not described (Kalle, G.P. 94075).

(v)  *$\alpha$ -Naphthol-3:6-disulphonic Acid* is technically the most important  *$\alpha$ -naphtholdisulphonic acid* and is obtained when sodium naphthalene-1:3:6-trisulphonic acid is heated

with 50% caustic soda solution at 170–180° (Gürke and Rudolph, G.P. 38281; B.P. 15716, 1885). It can be prepared from  $\alpha$ -naphthylamine-3:6-disulphonic acid, either by the diazo-reaction, or by heating its acid sodium salt with water under pressure at 180° (Cassella, G.P.a. 4375), or from  $\alpha$ -naphthol-3:6:8-trisulphonic acid by reduction with sodium amalgam (Bayer, G.P. 255724; B.P. 28172, 1911).

**Identification.**—The acid barium salt,  $\text{BaH}_2\text{A}_2$ , is sparingly soluble; the acid sodium salt,  $\text{NaHA}$ , is readily soluble in water or alcohol and gives a blue coloration with ferric chloride.

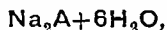
**Reaction.**—It couples with diazotised bases furnishing *ortho*-azo dyes. Heated with ammonia at 160° it gives 2-amino-4-naphthol-7-sulphonic acid mixed with 1:3-diaminonaphthalene-6-sulphonic acid, or with aniline at 160° the *diphenyl* derivative of the latter.

(vi)  $\alpha$ -Naphthol-3:7-disulphonic Acid can be prepared from  $\alpha$ -naphthylamine-3:7-disulphonic acid, either by the diazo-reaction, or by heating its acid sodium salt with water under pressure at 180°; or from  $\alpha$ -naphthol-3:5:7-trisulphonic acid by reduction with zinc dust and dilute caustic soda (Kalle, G.P. 233934).

**Reactions.**—The acid couples with diazotised bases. With ammonia at 160° it yields 2-amino-4-naphthol-6-sulphonic acid, mixed with 1:3-diaminonaphthalene-7-sulphonic acid, or with aniline, at 160°, the *diphenyl* derivative of the latter.

(vii)  $\alpha$ -Naphthol-3:8-disulphonic Acid is prepared from  $\alpha$ -naphthylamine-3:8-disulphonic acid by heating its acid sodium salt with water under pressure at 180° (Höchst, G.P. 71494; B.P. 14301, 1892).

**Identification.**—The sodium salt,



long prisms, soluble in 5.5 parts of cold water, gives with ferric chloride a deep blue coloration and with nitric acid yields, not a Naphthol Yellow, but oxidation products.

**Reactions.**—It couples with diazo-compounds forming *ortho*-azo dyes. Digested with 50% caustic soda at 170–210° it forms 1:8-dihydroxynaphthalene-3-sulphonic acid. Reduced with sodium amalgam, it yields  $\alpha$ -naphthol-3-sulphonic acid. Heated with ammonia at 160–180° it gives 1:3-diaminonaphthalene-8-sulphonic acid or with aniline and aniline hydrochloride at 150–170° the *diphenyl* derivative of this acid.

Naphthasultone-3-sulphonic acid is obtained from  $\alpha$ -naphthol-3:8-disulphonic acid by dehydration with sulphuric acid at 100°, or with phosphorus pentoxide or phosphorus pentachloride (Badische, G.P. 55094). The sulphonyl chloride (m.p. 190–191°) is obtained by interaction with chlorosulphonic acid (Gebauer-Fülneegg *et al.*, J. Amer. Chem. Soc. 1931, 53, 2648), which with ammonia gives  $\alpha$ -naphthol-3:8-disulphonamide (B.D.C., B.P. 296458). The acid forms readily soluble silky needles; the barium salt sparingly soluble long needles; the sodium salt,  $\text{NaA} + 3\text{H}_2\text{O}$ , long needles soluble in about 93 parts of cold water. It gives no coloration with ferric chloride and is readily hydrolysed by mineral acids or by alkalis (Ewer and Pick, G.P. 52724).

$\alpha$ -Naphthol-8-sulphonamide-3-sulphonic Acid is prepared by action of ammonia on naphthasultone-3-sulphonic acid. The acid, its barium salt,  $\text{BA}_2 + 5\text{H}_2\text{O}$ , and sodium salt,  $\text{NaA} + \text{H}_2\text{O}$ , are moderately soluble. With diazotised bases it couples, giving *ortho*-azo dyes which, when boiled with alkalis, give *peri*-anhydrides (sultams), the colour changing from bluish-red to yellow (Bernsthen, Ber. 1890, 23, 3094).

(viii)  $\alpha$ -Naphthol-4:6-disulphonic Acid can be prepared from  $\alpha$ -naphthylamine-4:6-disulphonic acid by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii], 70, 347), or by sulphonation of  $\alpha\alpha'$ -dinaphthyl carbonate with 20% oleum at 10–20°, hydrolysing the tetrasulpho- $\alpha\alpha'$ -dinaphthyl carbonate with dilute acid at 60–70° and separating the less soluble 4:7-disulphonic acid from the more soluble 4:6-acid by salting out (Höchst, B.P. 80888; B.P. 14134, 1894).

**Reactions.**—It gives azo-dyes on coupling, and a Naphthol Yellow when boiled with nitric acid.

(ix)  $\alpha$ -Naphthol-4:7-sulphonic Acid is a product, along with the 2:7-acid, of direct sulphonation of  $\alpha$ -naphthol with a relatively small proportion (2–3 parts) of sulphuric acid (approximately 93% strength) at 125–130°. It may be prepared from  $\alpha$ -naphthylamine-4:7-disulphonic acid by the bisulphite method, or from  $\alpha$ -chloronaphthalene-4:7-disulphonic acid by digestion with 30% caustic soda at 200–210° (Oehler, G.P. 74744); or by hydrolysing the product of tetrasulphonation of  $\alpha\alpha'$ -dinaphthyl carbonate (Höchst, *l.c.*).

**Identification.**—The barium salt,  $\text{BaA} + 4\text{H}_2\text{O}$ , and sodium salt,  $\text{Na}_2\text{A} + 4\text{H}_2\text{O}$ , are crystalline. The latter gives a blue coloration with ferric chloride.

**Reactions.**—It couples to give *ortho*-azo dyes. With nitrous acid it gives a very soluble nitroso-compound. Nitric acid forms 2:4-dinitro- $\alpha$ -naphthol-7-sulphonic acid. Boiled with 65% sulphuric acid, or with hydrochloric acid, it yields  $\alpha$ -naphthol-7-sulphonic acid.

(x)  $\alpha$ -Naphthol-4:8-disulphonic Acid is prepared from naphthasultone by heating with sulphuric acid at 80–90° until soluble in water (Bernsthen, Ber. 1890, 23, 3090), or from  $\alpha$ -naphthylamine-4:8-disulphonic acid by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii], 69, 80).

**Identification.**—The barium salt is sparingly soluble; the sodium salt,  $\text{Na}_2\text{A} + \text{H}_2\text{O}$ , forms very soluble scales which, with ferric chloride, give a deep blue coloration.

**Reactions.**—It couples with diazotised bases to give *ortho*-azo dyes. Nitrous acid gives the 2-nitroso derivative (Dressel and Kothe, Ber. 1894, 27, 2145). Nitric acid converts it into 2:4-dinitro- $\alpha$ -naphthol-8-sulphonic acid.  $\alpha$ -Naphthylamine-4:8-disulphonic acid can be produced by interaction with ammonia and bisulphite. On dehydration with cold 5% oleum it gives naphthasultone-4-sulphonic acid, but with 25% oleum below 100°,  $\alpha$ -naphthol-2:4:8-trisulphonic acid is produced. Chlorosulphonic acid converts it into naphthasultone-4-sulphonyl chloride, m.p. 195° (Gebauer-Fülneegg *et al.* J. Amer. Chem. Soc. 1931, 53, 2648). Fusion

with caustic soda at 250° gives 1:8-dihydroxy-naphthalene-4-sulphonic acid.

*Naphthasultone-4-sulphonic Acid* is formed as indicated above. The barium salt is easily soluble; the sodium salt (+3H<sub>2</sub>O), moderately soluble scales, is converted readily into *a-naphthol-4:8-disulphonate* by alkalis in the cold, or into the acid by boiling with dilute (5%) sulphuric acid, or, on prolonged boiling, by water alone. It gives neither a coloration with ferric chloride, nor does it couple with diazotised bases.

*a-Naphthol-8-sulphonamide-4-sulphonic Acid* is precipitated as its crystalline sodium salt (+2H<sub>2</sub>O) on acidification of a solution of the sultonesulphonate in ammonia. It is hydrolysed to the sultone or the disulphonic acid by boiling dilute acid (Badische, G.P. 57856). Coupled with diazotised bases it forms *ortho-azo* dyes closely resembling those obtained from the 8-sulphonamide-3-sulphonic acid (Geigy, G.P. 139287).

(xi) *a-Naphthol-5:7-disulphonic Acid* has not been described. It is mentioned as producible from and convertible into the *a-naphthylamine-5:7-disulphonic acid* by the bisulphite reaction (Badische, G.P. 115335; 117471; B.P. 1387, 1900).

(xii) *a-Naphthol-5:8-disulphonic Acid* has been obtained from *a-naphthylamine-5:8-disulphonic acid* by the diazo-reaction, the sultone first formed being converted, by alkali, into the disulphonic acid (Bayer, G.P. 70357).

*Naphthalsultone-5-sulphonic acid* forms a sodium salt, NaA + 1½H<sub>2</sub>O, needles, moderately soluble (Gattermann, Ber. 1899, 32, 1158) which, when digested with 40% caustic soda under pressure at 170–200°, yields 1:8-dihydroxynaphthalene-4-sulphonic acid (Bayer, G.P. 80667; B.P. 1227, 1894).

(xiii) *a-Naphthol-6:8-disulphonic Acid* may be prepared from *a-naphthylamine-6:8-disulphonic acid* by the bisulphite reaction (Bucherer, J. pr. Chem. 1904, [ii], 70, 347). It is also formed by hydrolysis, with 3% acid at 180–200°, of *a-naphthylamine-4:6:8-trisulphonic acid* (Kalle, G.P. 82563) or *a-naphthol-4:6:8-trisulphonic acid*. The acid sodium salt forms easily soluble short needles and, with ferric chloride, gives a fleeting green coloration.

*Reactions.*—It couples with diazotised bases forming azo-dyes. With nitrous acid, it yields a nitroso derivative which is not convertible into a Naphthol Yellow by nitric acid. With 50% caustic soda at 170–210° it gives 1:8-dihydroxynaphthalene-3-sulphonic acid.

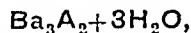
The corresponding naphthasultone-6-sulphonic acid and *a-naphthol-8-sulphonamide-6-sulphonic acid* have not been fully characterised.

#### *a-NAPHTHOLTRISULPHONIC ACIDS.*

(i) *a-Naphthol-2:4:7-trisulphonic Acid* is the chief product of sulphonation of *a-naphthol* with 25% oleum at 100–110° (Badische, G.P. 10785; B.P. 5305, 1879) from which it may be isolated by means of the barium salt (Friedländer and Taussig, Ber. 1897, 30, 1463). The trisulphonyl chloride of this acid is also obtained by prolonged action of excess of chlorosulphonic acid on *a-naphthol* at room temperature

(Gebauer-Fülnegg *et al.*, Monatsh, 1929, 53–54, 101). The acid is formed when *a-chloronaphthalene-2:4:7-trisulphonic acid* is heated with 12% caustic soda under pressure at 150° (Oehler, G.P. 77996).

*Identification.*—The barium salt,



glistening minute crystals, is almost insoluble when once separated from water; the other salts are easily soluble. The sodium salt gives a blue coloration with ferric chloride, but yields neither azo-dyes nor a nitroso-compound.

*Reactions.*—Nitric acid converts it into 2:4-dinitro-*a-naphthol-7-sulphonic acid*. Fusion with caustic soda produces 1:7-dihydroxynaphthalene-disulphonic acid. Reduced with sodium amalgam in the cold it gives *a-naphthol-2:7-disulphonic acid*. When heated with 66% sulphuric acid it yields *a-naphthol-7-sulphonic acid*.

(ii) *a-Naphthol-2:4:8-trisulphonic Acid* has been prepared by sulphonating *a-naphthol-4:8-disulphonic acid* or its sultone with 25% oleum below 100° (Bayer, B.P. 3397, 1890; Dressel and Kothé, Ber. 1894, 27, 2143).

*Identification.*—The sodium salt (+1½H<sub>2</sub>O), a readily soluble crystalline solid, showing a green fluorescence in solution, gives a blue coloration with ferric chloride but does not couple with diazotised bases.

*Reactions.*—Nitration at 20° with mixed acid gives 2:4-dinitro-*a-naphthol-8-sulphonic acid*. On reduction with sodium amalgam in the cold it gives *a-naphthol-2:4-disulphonic acid*. Fusion with caustic soda at 210° converts it into 1:8-dihydroxynaphthalene-2:4-disulphonic acid.

(iii) *a-Naphthol-3:5:7-trisulphonic Acid* is obtained, either from naphthalene-1:3:5:7-tetrasulphonic acid, by digestion with 15% caustic soda solution under pressure at 180° (Bayer, G.P. 79054; B.P. 25074, 1893), or from *a-naphthylamine-3:5:7-trisulphonic acid* by the diazo-reaction.

*Reactions.*—In neutral or alkaline solution it combines with tetrazo derivatives of the diphenyl series forming salts (Bayer, G.P. 92169; B.P. 8995, 1895). Reduced with zinc dust in boiling caustic soda, *a-naphthol-3:7-disulphonic acid* is produced. Heated with ammonia at 160–180°, it gives 1:3-diaminonaphthalene-5:7-disulphonic acid. Fused with 50% caustic soda at 150–160° it yields 1:5-dihydroxynaphthalene-3:7-disulphonic acid but with 60% caustic soda, 1:3-dihydroxynaphthalene-5:7-disulphonic acid is produced in addition.

(iv) *a-Naphthol-3:6:8-trisulphonic Acid*, the only technically important *a-naphthol*trisulphonic acid, is formed from *a-naphthylamine-3:6:8-trisulphonic acid*, either by the diazo-reaction, the sultone being an intermediate product (Koch, G.P. 56058; B.P. 9258, 1890), or by heating it with water under pressure at 180–250° (Höchst, G.P. 71495; B.P. 14301, 1892).

*Reactions.*—Coupled with diazotised bases, it forms dyes. Reduced with sodium amalgam in the cold it gives *a-naphthol-3:6-disulphonic acid*. Heated with ammonia at 160–180° it forms 1:3-diaminonaphthalene-6:8-disulphonic acid, or with aniline at 150–170°, the diphenyl



derivative of the same acid. Fused with 60% caustic soda at 170–220°, it yields the important 1:8-*dihydroxynaphthalene* - 3:6-*disulphonic acid* (Chromotropic Acid).

Its sultone gives yellow solutions with alkalis. Dissolved in ammonia, the sodium sultone-sulphonate, when mixed with hydrochloric acid, yields sodium *α*-naphthol-8-sulphonamide-3:6-disulphonate (Höchst, G.P. 69518), which couples to form dyes.

(v) *α*-Naphthol-4:6:8-trisulphonic Acid can be prepared from *α*-naphthylamine-4:6:8-trisulphonic acid, either by the diazo-reaction, with intermediate formation of the sultone, or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii], 70, 347).

**Reactions.**—Hydrolysed with 3% hydrochloric acid at 160–200° it gives *α*-naphthol-6:8-disulphonic acid. Fused with 70% caustic soda at 170–190° it yields 1:8-*dihydroxynaphthalene*-3:5-disulphonic acid.

Its sultone is easily soluble, forming colourless non-fluorescent solutions which with alkalis become deep yellow. The corresponding *α*-naphthol-8-sulphonamide-4:6-disulphonic acid couples with diazotised bases giving *ortho*-azo dyes.

#### HALOGENO-*α*-NAPHTHOLS.

Chlorination of *α*-naphthol gives only homonuclear derivatives. If chlorine is passed into a cooled acetic acid solution of *α*-naphthol, 2:4-dichloro-*α*-naphthol is formed (Cleve, Ber. 1888, 21, 891), followed by production of the additive compounds trichloro- and pentachloro-*α*-ketodi- and -tetrahydro-naphthalene (Zincke and Kegel, *ibid.* 1888, 21, 1031).

The halogens in halogenated naphthols, except when present in position 6 and 7, are removable by aqueous alcoholic stannous chloride in an atmosphere of nitrogen (Sampey, J. Amer. Chem. Soc. 1927, 49, 2849).

3-Chloro-*α*-naphthol has been prepared from 3-chloro-*α*-naphthylamine by the diazo-reaction (Hodgson and Elliott, J.C.S. 1934, 1705). It melts at 143°. Treated with bromine, it gives 3-chloro-2:4-dibromo-*α*-naphthol, m.p. 112°. In the same paper the 3-bromo- (m.p. 61°) and the 3-iodo- (m.p. 119°) *α*-naphthols are described.

4-Chloro-*α*-naphthol may be obtained by chlorinating either *α*-naphthyl carbonate (Reverdin and Kauffmann, Ber. 1895, 28, 3051) or *α*-naphthyl toluene-*p*-sulphonate in carbon tetrachloride (Aktienges., G.P. 240038). It may also be prepared from *α*-naphthol by chlorination with sulphuryl chloride (Kast, Ber. 1911, 44, 1337), but when the naphthol, dissolved in alkali, is chlorinated by hypochlorous acid (Kalle, G.P. 167458) the product is not pure. It sublimes in long needles, m.p. 117–118°, dissolves readily in alcohol or benzene, gives a blue precipitate with ferric chloride and couples with diazotised bases.

2-Bromo-*α*-naphthol, from 2-bromo *α*-naphthylamine, has m.p. 45° (Hodgson and Hathway, J.C.S. 1944, 538).

6- and 7-Bromo-*α*-naphthols have been synthesised, by the Erdmann method, from *m*- and *p*-bromophenylparaconic acids, themselves

synthesised from *m*- and *p*-bromobenzaldehyde and succinic anhydride (Fuson, J. Amer. Chem. Soc. 1925, 47, 516).

**Chloro-*α*-naphtholsulphonic Acids.**—Four, namely the 6- and 7-chloro-*α*-naphthol-3-sulphonic acids, the 6-chloro-*α*-naphthol-3:5- and the 8-chloro-*α*-naphthol-3:6-disulphonic acids, formed from the corresponding aminonaphthol-mono- and di-sulphonic acids by the Sandmeyer reaction, have been proposed for coupling with diazotised dehydrothiotoluidine in the production of *ortho*-azo dyes (Bayer, G.P. 96768; B.P. 9441, 1894).

8-Chloro-*α*-naphthol-3:6-disulphonic acid, obtained by heating 8-chloro-*α*-naphthylamine-3:6-disulphonic acid with dilute sulphuric acid under pressure (Badische, G.P. 147852), is a crystalline, deliquescent solid. Its acid barium salt, BaH<sub>2</sub>A<sub>2</sub>·6H<sub>2</sub>O, crystallises in needles; acid potassium salt in scales; acid sodium salt in needles. The normal salts are readily soluble, give non-fluorescent solutions which, with ferric chloride, give a dark green coloration. Compared with the azo-dyes from *α*-naphthol-3:6-disulphonic acid, those from this *perchloro*-acid are much bluer in shade and of enhanced fastness (Cassella, G.P. 82285; 99227).

**NITROSO-*α*-NAPHTHOLS** (see *Naphthaquinone-oximes*, p. 385a).

#### NITRO-*α*-NAPHTHOLS.

*α*-Naphthol, nitrated in acetic acid below 7°, gives a 34% yield of 2-nitro-*α*-naphthol. If the acetyl derivative is similarly nitrated the yield of 2-nitro-*α*-naphthol is 45% and some 2:4-dinitro-*α*-naphthol is produced. The 4-nitro derivative is the chief constituent of the product of nitration of the methyl ether under similar conditions (Hodgson and Smith, J.C.S. 1935, 671). But nitro-*α*-naphthols are commonly obtained from naphtholsulphonic acids, nitroso-naphthols, or nitrosonaphtholsulphonic acids containing the nitroso-group, or at least one sulphonic group, in the same nucleus as the hydroxyl group. A method, of no technical importance, from *α*-chloronitronaphthalenes, has been used to prepare 4-mono-, the 2:4-di- and the 2:4:5- and 2:4:8-tri-nitro-*α*-naphthols.

The nitro-*α*-naphthols containing a nitro-group in the *ortho*-position to the hydroxyl radical dye wool and silk in various shades of yellow.

(i) 2-Nitro-*α*-naphthol, as already described, is a product of nitration of *α*-naphthol. It may be prepared from 2-nitroso-*α*-naphthol by oxidation with diluted nitric acid in the cold, or better with hydrogen peroxide; or from acet-*α*-naphthalide by nitration, the 2-nitro-*α*-naphthol being separated, after hydrolysis by boiling with 5% caustic soda solution, by distillation in steam (Hodgson and Kilner, *ibid.* 1924, 125, 807).

**Properties.**—It crystallises in greenish-yellow plates, m.p. 128°, is sparingly soluble in dilute alcohol and only very slightly in water. It is volatile in steam and forms dark red salts with alkalis. Its *acetate*, bright-yellow needles, melts at 118°; the *ethyl ether*, also bright-yellow needles, melts at 84°.



(ii) 3-Nitro- $\alpha$ -naphthol, yellow needles, m.p. 167–168° (see Veselý and Dvorský, *Bull. Soc. chim.* 1923, [iv], 33, 329).

(iii) 4-Nitro- $\alpha$ -naphthol (*French Yellow*, *Campobello Yellow*; *Chrysæic Acid*) is formed when bis-4-nitro- $\alpha$ -naphthyl carbonate, m.p. 212°, is heated with alcoholic potash (Reverdin and Kauffmann, *Ber.* 1895, 28, 3050); or when 4-nitro- $\alpha$ -chloronaphthalene is heated with aqueous sodium carbonate under pressure at 150–155° (Greisheim, *G.P.* 117731; *B.P.* 7692, 1900). The nitration of  $\alpha$ -naphthyl *m*-nitrobenzenesulphonate with fuming nitric acid in acetic acid yields a mixture of 4- and 8-nitro-compounds (Bell, *J.C.S.* 1933, 286).  $\alpha$ -Naphthyl methyl ether, nitrated in acetic acid below 7°, gives mainly the 4-nitro-product (Hodgson and Smith, *l.c.*).

*Properties.*—It crystallises from hot water in golden-yellow needles, m.p. 164°, readily soluble in alcohol or acetic acid; it is not volatile in steam. The salts are orange-red to dark red in colour, readily soluble in water; the sodium salt,  $\text{NaA} + 2\text{H}_2\text{O}$ , carmine-red needles, was formerly used as a yellow dye for silk or wool. The methyl ether melts at 85–86° (81°), the ethyl ether at 116–117° (120°). On nitration it yields 2:4-dinitro- $\alpha$ -naphthol, but the 4-nitro- $\alpha$ -naphthyl *m*-nitrobenzenesulphonate yields the 4:5-dinitro derivative (Bell, *l.c.*).

(iv) 5-Nitro- $\alpha$ -naphthol obtained from 5-nitro- $\alpha$ -naphthylamine, by the diazo-reaction, separates from hot water in dark yellow crystals, m.p. 165°; gives an acetate, needles, m.p. 114°, and benzoate, m.p. 109°; couples with diazotised bases, and, with nitrous acid, yields 5-nitro-4-nitroso- $\alpha$ -naphthol (Kaufler and Brauer, *Ber.* 1907, 40, 3271; Fichter and Kühnel, *ibid.* 1909, 42, 4751).

(v) 6-Nitro- $\alpha$ -naphthol, yellow plates, m.p. 181–182° (Hodgson and Turner, *J.C.S.* 1944, 8).

(vi) 8-Nitro- $\alpha$ -naphthol, m.p. 130°, may be isolated from the product of nitration of  $\alpha$ -naphthyl *m*-nitrobenzenesulphonate (Bell, *l.c.*).

#### DINITRO- $\alpha$ -NAPHTHOLS.

(i) 2:4-Dinitro- $\alpha$ -naphthol (*Martius Yellow*, *Manchester Yellow*, *Naphthalene Yellow*, *Naphthol Yellow*) is a product of the action of nitric acid on  $\alpha$ -naphthol, 2-nitroso-, and 4-nitroso- $\alpha$ -naphthol, 2-nitro- and 4-nitro- $\alpha$ -naphthol, and on  $\alpha$ -naphthol-2-sulphonic acid,  $\alpha$ -naphthol-4-sulphonic acid,  $\alpha$ -naphthol-2:4-disulphonic acid (Bender, *Ber.* 1889, 22, 996), or 1-ethoxynaphthalene-4-sulphonic acid (Witt and Schneider, *ibid.* 1901, 34, 3186). It is also formed when  $\alpha$ -naphthylamine is heated with concentrated nitric acid, or nitrous fumes are led into an ethereal solution of  $\alpha$ -naphthol at 0° (Schmidt, *ibid.* 1900, 23, 3245).

*Preparation.*—Either  $\alpha$ -naphthol-2:4-disulphonic acid, made by sulphonating  $\alpha$ -naphthol with twice its weight of sulphuric acid below 50°, is heated with dilute nitric acid at 100°, or the two  $\alpha$ -naphtholmonosulphonic acids, formed when  $\alpha$ -naphthol is sulphonated under Schaffer's conditions (*Annalen*, 1869, 152, 293), are converted into their nitroso derivatives by interaction with sodium nitrite and sulphuric acid in

the cold, and the product finally warmed with nitric acid.

*Properties.*—It crystallises from alcohol in citron-yellow needles, m.p. 138°, does not volatilise with steam and is sparingly soluble in alcohol, ether, and benzene. It is an acid, dissolving in sodium carbonate solution, and forms soluble, orange-coloured salts (Korezynski, *Ber.* 1903, 42, 174). The sodium salt,  $\text{NaA} + \text{H}_2\text{O}$ , ammonium salt,  $\text{NH}_4\text{A} + \text{H}_2\text{O}$ , and calcium salt,  $\text{CaA}_2 + 6\text{H}_2\text{O}$ , crystallise in needles, and were formerly used as golden-yellow dyes for silk and wool. Dinitro- $\alpha$ -naphthol, however, has little affinity for the fibre, being removed from it either by volatilisation or by washing.

*Reactions.*—With nitric acid in sulphuric acid below 50°, it yields a mixture of 2:4:5- and 2:4:7-trinitro- $\alpha$ -naphthols. Prolonged boiling with concentrated nitric acid oxidises it to phthalic and oxalic acids. With cold hypochlorite it gives first 2-chloro-[ $\alpha$ ]naphthaquinone and finally phthalic and oxalic acids. Digested with alcoholic ammonia at 190–200°, it yields 2:4-dinitro- $\alpha$ -naphthylamine. With potassium cyanide in hot alcoholic solution, naphthylpurpuric acid is formed and with toluene-*p*-sulphonyl chloride and diethylaniline, 4-chloro-1:3-dinitronaphthalene is obtained (Ullmann and Bruck, *ibid.* 1908, 41, 3932).

(ii) 4:5-Dinitro- $\alpha$ -naphthol, mixed with the 4:8-dinitro- $\alpha$ -naphthol, is obtained from the product of nitration of  $\alpha$ -naphthyl *m*-nitrobenzenesulphonate with fuming nitric acid in acetic acid (Bell, *J.C.S.* 1933, 286). It is prepared by oxidation of 5-nitro-4-nitroso- $\alpha$ -naphthol with alkaline ferri-cyanide solution. It crystallises in yellow needles, m.p. 230°, is only sparingly soluble in water and has feeble dyeing properties (Friedländer, *Ber.* 1899, 32, 3529). The methyl ether, m.p. 216°, and ethyl ether, scales, m.p. 182°, have been described (Ullmann and Consonno, *ibid.* 1902, 35, 2808).

(iii) 4:8-Dinitro- $\alpha$ -naphthol may be obtained as above or by oxidation of the corresponding 8-nitro-4-nitroso- $\alpha$ -naphthol and has m.p. 135°.

#### TRINITRO- $\alpha$ -NAPHTHOLS.

(i) 2:4:5-Trinitro- $\alpha$ -naphthol (*Naphthopicroic acid*) is formed when 5-nitro-4-nitroso- $\alpha$ -naphthol is warmed with dilute nitric acid (Graebe and Oeser, *Annalen*, 1904, 335, 147; cf. *J.S.C.I.* 1900, 19, 339); or, mixed with the 2:4:7-trinitro derivative, when 2:4-dinitro- $\alpha$ -naphthol is nitrated in the cold with nitrosulphuric acid (Kehrmann and Haberkant, *Ber.* 1898, 31, 2421).

*Properties.*—It forms needles, m.p. 190°, and its potassium salt,  $\text{KA} + \text{H}_2\text{O}$ , needles, is easily soluble in hot, sparingly in cold water. It is a strong acid, dyes wool yellow, yields 3-nitrophthalic acid on oxidation and gives 4-chloro-1:3:8-trinitronaphthalene when heated with toluene-*p*-sulphonyl chloride and diethylaniline.

(ii) 2:4:7-Trinitro- $\alpha$ -naphthol is the more soluble isomer obtained when 2:4-dinitro- $\alpha$ -naphthol is nitrated in the cold with nitrosulphuric acid (Kehrmann and Haberkant, *l.c.*), and is freed from the 2:4:5-compound by con-

version into the sparingly soluble sodium salt (Kehrmann and Steiner, *ibid.* 1900, 33, 3286).

*Properties.*—It forms yellow needles, m.p. 145°, but, from benzene or acetic acid, prisms, containing solvent, which effloresce in the air. On oxidation it yields 4-nitrophthalic acid. The *potassium* salt is easily, but the *sodium* salt, yellow needles, only sparingly soluble in water.

(iii) 2:4:8-Trinitro- $\alpha$ -naphthol, obtained by mixing 8-nitro-4-nitroso- $\alpha$ -naphthol with 50% nitric acid in the cold (Graebe and Oeser, *Annalen*, 1904, 335, 156) forms yellow prisms, m.p. 175°. It dyes wool yellow.

(iv) 4:5:7-(or 4:6:8-)Trinitro- $\alpha$ -naphthol has not been isolated, but its methyl ether is formed by the interaction of 1:3:5:8-tetranitronaphthalene and sodium methoxide. This ether crystallises in yellow needles, m.p. 186°, and on oxidation yields 3:5-dinitrophthalic acid (Will, *Ber.* 1895, 28, 372).

#### TETRANITRO- $\alpha$ -NAPHTHOL.

2:4:5:7-Tetranitro- $\alpha$ -naphthol (*Heliochrysin*) is obtained by digesting tetranitro- $\alpha$ -bromonaphthalene (m.p. 170.5°) with warm, concentrated aqueous sodium carbonate (Merz and Weith, *ibid.* 1882, 15, 2714). It crystallises in yellow scales, m.p. 180°, and forms reddish-yellow salts which dissolve only sparingly in water. The *potassium* salt,  $KA + 1\frac{1}{2}H_2O$ , prisms, is soluble in 340 parts, and the *sodium* salt,  $NaA + 2H_2O$ , scales, in about 94 parts of water at 19°. It dyes silk and wool golden-yellow, but has no technical value.

#### NITRO- $\alpha$ -NAPHTHOLSULPHONIC ACIDS.

(i) 2-Nitro- $\alpha$ -naphthol-4-sulphonic Acid can be obtained from the corresponding ethyl ether by hydrolysis with caustic potash solution. The *basic barium* salt,  $BaA + H_2O$ , is very sparingly soluble; the yellow *potassium* and orange *basic potassium* salts form needles easily soluble in water. When its salts are heated with hydrochloric acid under pressure at 150–160°, 2-nitro- $\alpha$ -naphthol is obtained (Witt and Schneider, *ibid.* 1901, 34, 3189).

(ii) 2-Nitro- $\alpha$ -naphthol-7-sulphonic Acid, formed from diazotised 2-nitro-4-amino- $\alpha$ -naphthol-7-sulphonic acid by decomposition in water with copper powder, crystallises with  $1H_2O$  in yellow needles. Its *copper* salt,  $CuA_2 + 5H_2O$ , forms greenish-yellow needles. On reduction it yields 2-amino- $\alpha$ -naphthol-7-sulphonic acid (Finger, *J. pr. Chem.* 1909, [ii], 79, 441).

(iii) 2:4-Dinitro- $\alpha$ -naphthol-7-sulphonic Acid (Naphthol Yellow S, Acid Yellow S) is formed by nitration of  $\alpha$ -naphthol-7-sulphonic acid (Bender, *ibid.* 1889, 22, 996), or of a mixture of  $\alpha$ -naphthol-2:7- and 4:7-disulphonic acids (Levinstein, *B.P.* 5692, 1882; Leonhardt, *B.P.* 11318, 1887), or of  $\alpha$ -naphthol-2:4:7-trisulphonic acid (Badische, *G.P.* 10785; Höchst, *G.P.* 22545; *B.P.* 2178, 1882).

*Preparation.*—(1) To the solution obtained by diluting the trisulphonation melt from  $\alpha$ -naphthol (10 kg.) with water to 100 litres, nitric acid,  $\rho$  1.38 (25 kg.) is added below 50°. From the solution dinitro- $\alpha$ -naphtholsulphonic acid

separates in needles, the mother-liquors containing other unidentified nitration products.

(2) The mixed  $\alpha$ -naphtholdisulphonic acids of Leonhardt's *B.P.* 11318, after conversion into nitroso-compounds by action of sodium nitrite, are nitrated at 50° with nitric acid in the proportion 25 kg. to every 10 kg. of  $\alpha$ -naphthol sulphonated.

*Salts.*—The acid crystallises from hydrochloric acid in yellow needles. The *barium* and *basic potassium*,  $K_2A$ , salts are very sparingly soluble; the *acid potassium*,  $KA$ , *basic sodium*,  $Na_2A$ , and *ammonium* salts are orange-yellow and readily soluble in water. It is a strong acid, possesses considerable tinctorial power and is used as a yellow dye for wool.

*Reactions.*—By oxidation with nitric acid ( $\rho$  1.35) it gives 4-sulphophthalic acid. With hypochlorite it is rapidly oxidised in the cold to 4-sulphophthalic acid and chloropicrin (Seyewetz and Chaise, *Bull. Soc. chim.* 1927, [iv], 41, 196). It may be reduced to yield 2-nitro-4-amino- $\alpha$ -naphthol-7-sulphonic acid (Finger, *l.c.*) by stannous chloride in hydrochloric acid, but, in ammoniacal solution with sodium sulphide, it gives the isomeric 4-nitro-2-amino- $\alpha$ -naphthol-7-sulphonic acid (Gesellsch., *G.P.* 189513; *B.P.* 7535, 1906).

(iv) 2:4-Dinitro- $\alpha$ -naphthol- $\beta$ -sulphonic Acid (Brilliant Yellow) is formed when the nitroso derivative of sodium  $\alpha$ -naphthol-8-sulphonic acid in dilute sulphuric acid solution is mixed with nitric acid in the cold, finishing at 100°; or when sodium  $\alpha$ -naphthol-2:4:8-trisulphonate, dissolved in sulphuric acid, is mixed with nitrosulphuric acid at 20° (Dressel and Kothe, *Ber.* 1894, 27, 2145).

*Properties.*—The *potassium* salt,  $KA + H_2O$ , and the *sodium* salt,  $NaA$ , form sparingly soluble yellow needles, and in an acid bath dye silk and wool a more orange shade than that produced with the isomeric 7-sulphonic acid. As a dyestuff it has no technical value.

#### $\beta$ -Naphthol.

$\beta$ -Naphthol (2-hydroxynaphthalene) is the most important technical intermediate product prepared from naphthalene. Not only is it used for the production of dyes and pigments by coupling with diazotised bases, but also for the manufacture of  $\beta$ -naphthylamine, of several  $\beta$ -naphtholsulphonic acids, and of the important 2:3-hydroxynaphthoic acid (*q.v.*). It is manufactured by fusing sodium naphthalene- $\beta$ -sulphonate with caustic soda.

*Manufacture.*—Caustic soda (10 parts) is melted with a small quantity of water, in a cast-iron vessel fitted with a stirrer, at 270–300°, and sodium naphthalene- $\beta$ -sulphonate (about 20 parts), which may contain a small proportion of water, is charged in over a period at the same temperature. The fusion is finished off at about 300° and the melt then dissolved in the minimum amount of water. At this stage some solid sodium sulphite may be recovered. The liquor is neutralised, finally acidified with sulphuric acid and then run off from the separated  $\beta$ -naphthol, which after being washed thoroughly

with water is then dried and distilled under reduced pressure. Instead of sulphuric acid, sulphur dioxide may be used to "split" the diluted caustic melt, the sulphur dioxide being generated by using recovered sodium sulphite to neutralise the sulphuric acid in the sulphonation of naphthalene. There is some tarry residue from the distillation; this is said to be increased by the presence of iron salts or  $\beta$ -sulphonate and especially by naphthalene- $\beta$ -sulphonic acid in the  $\beta$ -naphthol (Troitzki and Blagovestschenski, *Prom. Org. Chem.* 1937, 3, 89).

To avoid oxidation, which occurs during alkali fusion of sulphonic acids in open vessels (Boswell and Dickson, *J. Amer. Chem. Soc.* 1918, 40, 1787), the fusion may be conducted in caustic soda solution of  $p$  1.384 in an autoclave at 300–330° for 10–12 hours (Aktienges., *F.P.* 469040, *J.S.C.I.* 1914, 33, 955), or with 10% caustic soda at 300° for 30 hours (Willson and Meyer, *Ber.* 1914, 47, 3162), or by adding hot (100°) concentrated aqueous solution of naphthalene- $\beta$ -sulphonate to fused caustic soda in a covered vessel at 300°. The addition of 1–2% sodium carbonate during fusion is said to prevent overheating and charring (Zakharov, *B.* 1929, 274). Oxidation is prevented by avoiding iron vessels and working under air-free conditions (May, *J. Amer. Chem. Soc.* 1922, 44, 650). The presence of sodium bisulphate in the crude naphthol leads to formation of  $\beta\beta'$ -dinaphthyl ether on distillation (Rodionov and Manzov, *J.S.C.I.* 1923, 42, 509r).

**Properties.**— $\beta$ -Naphthol crystallises in scales or rhombic tables, m.p. 122.0–122.2°, b.p. 294.85°/760 mm. (Berliner, May and Lynch, *J. Amer. Chem. Soc.* 1927, 49, 1012). It is readily soluble in organic solvents or in aqueous caustic alkali solution; sparingly soluble in hot water. It sublimes, and can be distilled in superheated steam. It has antiseptic properties. The sodium, m.p. 120°, and potassium naphthoxide, m.p. 38–40°, crystallise in scales (McL drum and Patel, *J. Indian Chem. Soc.* 1928, 5, 91).

**Reactions.**— $\beta$ -Naphthol couples readily with diazotised bases and is used as an end component for the production of azo-dyes, either in substance or on the fibre. With nitrous acid it forms nitroso- $\beta$ -naphthol (see naphthaquinone oximes, p. 385a), or, in ethereal solution, 1:6-dinitro- $\beta$ -naphthol, which is also a product of direct nitration in acetic acid (Bell, *J.C.S.* 1932, 2732). By sulphonation, mono-, di-, and tri-sulphonic acids may be prepared. Distilled with zinc dust it yields  $\beta$ -dinaphthylene oxide (Brass and Patzelt, *Ber.* 1937, 70 [B], 1349).

Oxidised with alkaline permanganate, it yields either *o*-carboxycinnamic acid or phthalonic acid (Henriques, *ibid.* 1888, 21, 1618), but fused with caustic alkali and copper oxide, or hydrated manganese peroxide, it gives phthalic and benzoic acids. When oxidised with peracetic acid, in 10% acetic acid at below 40°, it yields 80% of *o*-carboxyallocinnamic acid (Böescken and von Königsfeldt, *Rec. trav. chim.* 1935, 54, 313). On oxidation with ferric chloride it yields 1:1'-di- $\beta$ -naphthol (*q.v.*), with intermediate formation of basic iron salts (Joffe, *J. Gen. Chem. Russ.* 1937, 7, 2710; *A.* 1938, 182).

Heated with ammonia and ammonium sulphite at 100–150° under pressure it yields  $\beta$ -naphthylamine—the reaction with ammonia can also be conducted catalytically over alumina at 430–445° (Howald and Lowy, *Ind. Eng. Chem.* 1923, 15, 397)—or with acetamide it yields acet- $\beta$ -naphthalide or with aniline *N*-phenyl- $\beta$ -naphthylamine. With  $\beta$ -aminoethyl alcohol in presence of aqueous sodium bisulphite at 90° it gives 5-hydroxyethyl-2-aminonaphthalene, m.p. 51° (*I.G.*, *B.P.* 442310).

Condensed with aldehydes, sulphur chloride, benzyl chloride, etc., it gives resinous compounds (*I.G.*, *B.P.* 327713; Bakelite, *B.P.* 468391). With dimethylolcarbamide it gives di- $\beta$ -naphthyl dimethylcarbamide, which, boiled with hydrochloric acid, yields  $\alpha\beta$ -di(2-hydroxy-1-naphthyl)ethane (De Dicsbach *et al.*, *Helv. Chim. Acta*, 1931, 14, 355).

$\beta$ -Naphthol condenses with carbon disulphide in presence of alkali and a solvent such as acetone to give 2-hydroxy-1-dithionaphthoic acid, m.p. 99°, which can be used as a rubber vulcanisation accelerator (Wingfoot Corp., *B.P.* 551305; *cf.* *U.S.P.* 2289649, 1942).

It forms basic salts when boiled in carbon tetrachloride with metallic chlorides such as  $WCl_2(OC_{10}H_7)_4$  with tungstic chloride (Funk and Baumann, *Z. anorg. Chem.* 1937, 231, 264). It gives molecular compounds with 1-chloro-2:4-dinitrobenzene, deep yellow crystals, m.p. 91°; with 2:4-dinitrotoluene, m.p. 74.5°; with trinitrobenzene, yellow needles, m.p. 158° (Buehler, Hisey, and Wood, *J. Amer. Chem. Soc.* 1930, 52, 1939).

**Colour Reactions.**—An aqueous solution of  $\beta$ -naphthol with bleaching-powder solution gives a pale yellow coloration disappearing on addition of excess; with ferric chloride solution, a pale green coloration changing to a white precipitate of  $\beta\beta'$ -dinaphthol. Warmed with strong caustic potash solution and chloroform at 50°, it gives a prussian blue coloration which gradually fades through green to brown. With sodium it gives (as distinct from  $\alpha$ -naphthol) a deep blue colour (Kunz-Krause, *Chem.-Ztg.* 1923, 47, 646).

**Tests.**—Commercial  $\beta$ -naphthol is a creamy white powder or flakes. Its crystallising point should not be below 120.5° and  $\alpha$ -naphthol content not above 0.1%.

**Estimation.**—This may be done either by titration in alkaline solution with a standard solution of a diazotised base, or by addition of excess standard iodine (a tri-iodo derivative is formed) to the alkaline solution and back titrating the excess iodine, after acidification, with sodium thiosulphate. For methods of estimating  $\alpha$ -naphthol in  $\beta$ -naphthol, see Callan, *J.S.C.I.* 1925, 44, 125.

$\beta$ -Naphthyl Methyl Ether (*Nerolin*), prepared by heating  $\beta$ -naphthol (5 parts) dissolved in absolute methyl alcohol (5 parts) with sulphuric acid (2 parts) forms scales, m.p. 72°, b.p. 274°, is sparingly soluble in alcohol and has an odour of orange flowers. It reacts with *o*-phthaloylchloride in carbon disulphide to give *o*-2-methoxy-1-naphthoylbenzoic acid, m.p. 195–196°; and in tetrachloroethane to give 1:8-phthalyl- $\beta$ -naphthol, m.p. 199–200° (Knapp, *Monatsh.* 1932, 60, 189).

$\beta$ -Naphthyl Ethyl Ether, prepared by reaction of  $\beta$ -naphthol with ethyl alcohol in presence of sulphuric acid, has m.p.  $37^\circ$ , b.p.  $282^\circ$ , is readily soluble in alcohol, and has an odour of pineapple. On nitration it yields 1-nitro- $\beta$ -ethoxynaphthalene, m.p.  $104^\circ$ , as major product, with some 6-nitro- $\beta$ -ethoxynaphthalene, m.p.  $114^\circ$  (Gaess, J. pr. Chem. 1891, [ii], 43, 22).

$\beta$ -Naphthyl Phenyl Ether, m.p.  $46^\circ$ , is obtained when a solution of sodium  $\beta$ -naphthoxide in  $\beta$ -naphthol is heated with chlorobenzene under pressure at  $200$ – $220^\circ$  (Fritzsch, G.P. 269543; B.P. 9797, 1913).

$\beta\beta'$ -Dinaphthyl Ether, m.p.  $105^\circ$ , is formed by boiling  $\beta$ -naphthol for some hours with 50% sulphuric acid (Graebe, Ber. 1880, 13, 1850), or by heating  $\beta$ -naphthol with phosphorus pentachloride (1 mol.) at  $100^\circ$  for 2 hours (Berger, Compt. rend. 1905, 141, 1027). Other ethers are described by Kirmer and Richter, J. Amer. Chem. Soc. 1929, 51, 3409. Many naphthyl ethers may be identified as picrates (see Dermer, J. Org. Chem. 1938, 3, 289).

$\beta\beta'$ -Dinaphthyl Carbonate, m.p.  $176$ – $177^\circ$ , obtained by action of phosgene on sodium  $\beta$ -naphthoxide, forms needles, sparingly soluble in alcohol. On sulphonation it yields a mixture of  $\beta$ -naphthol-6-, -7-, and -8-sulphonic acids (Reverdin and Kauffmann, Ber. 1895, 28, 3057).

$\beta\beta'$ -Dinaphthyl Sulphite is obtained when  $\beta$ -naphthol dissolved in carbon disulphide is heated with thionyl chloride in presence of pyridine (Badische, G.P. 303033).

$\beta$ -Naphthyl Acetate, m.p.  $70^\circ$ , obtained by heating  $\beta$ -naphthol with acetyl chloride, or with acetic acid at  $240^\circ$ , is sparingly soluble in water and is hydrolysed on distillation in steam (see Leman, Compt. rend. 1936, 202, 579).

$\beta$ -Naphthyl esters of aromatic carboxylic acids by interaction with acid condensing agents, such as aluminium chloride, are converted into  $\alpha$ -aroyl- $\beta$ -naphthols; thus  $\beta$ -naphthyl benzoate gives 1-benzoyl-2-naphthol (Höchst, B.P. 248791).

#### $\beta$ -NAPHTHOLSULPHONIC ACIDS.

The common method for the preparation of the greater number of the  $\beta$ -naphtholsulphonic acids is sulphonation of  $\beta$ -naphthol. With a limited proportion of sulphuric acid the first product at low temperatures is  $\beta$ -naphthol-1-sulphonic acid. With temperature rising to  $50$ – $60^\circ$ , the 6-, 7-, and 8-sulphonic acids are formed, the 8-acid predominating, the 7- only in traces. At  $90$ – $100^\circ$  the  $\beta$ -naphthol-6-sulphonic acid predominates. Using a larger proportion of sulphuric acid, disulphonic acids are formed, the 6:8-disulphonic acid predominating at lower temperatures ( $60$ – $80^\circ$ ), the 3:6-disulphonic acid at higher temperatures ( $120$ – $130^\circ$ ), but the reaction always produces a mixture in which  $\beta$ -naphthol-6-sulphonic acid is never completely absent. Under still more drastic conditions, using an excess of 20% oleum, first the 3:6:8-trisulphonic acid and later the 1:3:7-trisulphonic acid and the 1:3:6:7-tetrasulphonic acids are produced (Vorontzov and Sokolova, B. 1937, 1018).

$\beta$ -Naphthol-7-sulphonic acid, which is best prepared from naphthalene-2:7-disulphonic acid by fusion with caustic soda, gives the 1:7- and 3:7-disulphonic acids on further sulphonation,

followed by the 1:3:7-trisulphonic acid and 1:3:6:7-tetrasulphonic acids on still more drastic sulphonation with oleum.

The composition of the mixtures of sulphonic acids formed is, to some extent, probably governed by an equilibrium, dependent on temperature, set up comparatively slowly. The relationship between these acids is shown in the scheme given on the opposite page. Despite the general rule of preferential substitution in the  $\alpha$ -position, the sulphonic acid radical is not found in either the 4- or 5-position in any of the products of sulphonation of  $\beta$ -naphthol. With reference to the 1-position, of the four acids obtained from  $\beta$ -naphthol-7-sulphonic acid by sulphonation, the three containing a sulphonic group in this position are formed under anhydrous conditions.

Sulphonation of  $\beta$ -naphthol with chlorosulphonic acid follows a different main route. At ordinary temperatures the chief monosulphonation product is  $\beta$ -naphthol-1-sulphonic acid; at  $130^\circ$ , in tetrachlorethane,  $\beta$ -naphthol-6-sulphonic acid. With excess of chlorosulphonic acid, at ordinary temperatures,  $\beta$ -naphthol-1:6- and 1:5-disulphonyl chlorides are formed; at  $130$ – $140^\circ$ ,  $\beta$ -naphthol-3:6:8-trisulphonyl chloride (Pollak, Gebauer-Fülnegg and Blumenstock-Halward, Monatsh. 1928, 49, 187; 1929, 53–54, 83; Pollak and Blumenstock-Halward, *ibid.* 1928, 49, 202).

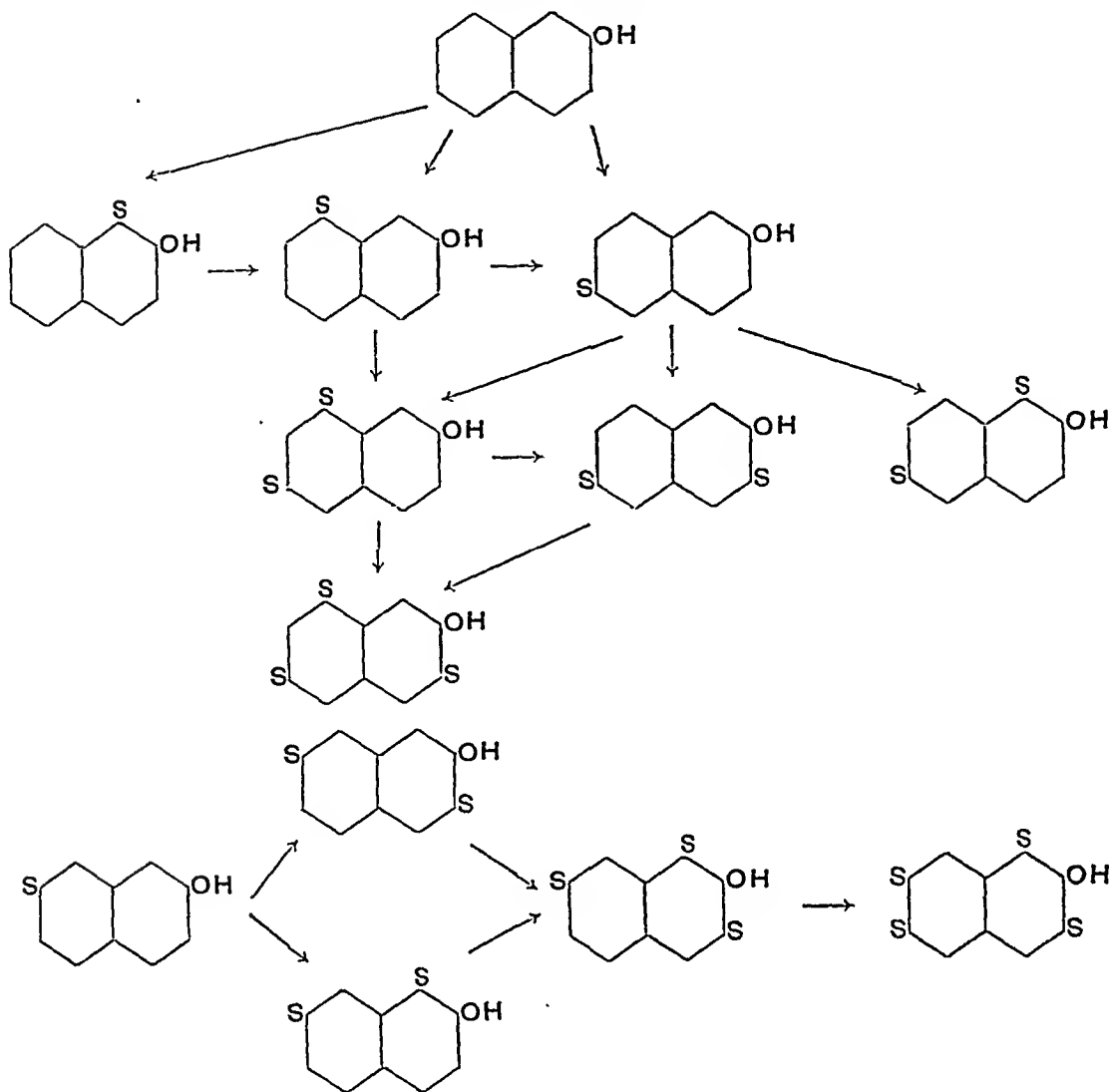
Addition of boric acid during sulphonation with sulphuric acid favours formation of the 1-sulphonic acid; 0.33 mol. of boric acid per mol. naphthol gives the maximum effect. Disulphonation at  $0^\circ$  in presence of boric acid gives the 1:6-disulphonic acid in good yield (Engel, J. Amer. Chem. Soc. 1930, 52, 2835; cf. Crossley and Simpson, U.S.P. 1570046).

Because sulphonic groups in an  $\alpha$ -position are preferentially replaced, the methods most widely used in preparation of  $\alpha$ -naphtholsulphonic acids cannot be applied generally to the preparation of  $\beta$ -naphtholsulphonic acids. Thus alkali fusion can only be used with naphthalene-2:6- and 2:7-disulphonic acids to prepare  $\beta$ -naphtholsulphonic acids. Further, exchange of the amino-group for hydroxyl is of limited use in the  $\beta$ -series because the  $\beta$ -naphthylaminesulphonic acids are themselves prepared from the  $\beta$ -naphtholsulphonic acids.

The  $\beta$ -naphtholsulphonates are well defined and comparatively easy to separate from mixtures. The formation of arylamine salts has been suggested as a special method of separation and characterisation, as these salts have sharp melting-points (Foster and Keyworth, J.S.C.I. 1927, 46, 297).

The chief uses of  $\beta$ -naphtholsulphonic acids are the preparation of  $\beta$ -naphthylaminesulphonic acids and in the manufacture of *ortho*-azo dyes. The position of the sulphonic groups affects the colour of the compounds formed on coupling with diazotised bases (see Crossley and Resenvelt, Ind. Eng. Chem. 1924, 16, 271).

$\beta$ -Naphtholsulphonic acids give tanning agents with halogenated aralkyl halides (I.G., B.P. 320056) and with formaldehyde (Badische, G.P. 409984; Deutsch.-Koloniale Gerb.- and Farbstoff-Ges., G.P. 306132).

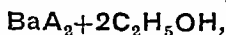


#### $\beta$ -NAPHTHOL MONOSULPHONIC ACIDS.

The technically valuable  $\beta$ -naphtholmonosulphonic acids are the 1-, 6-, 7-, and 8-isomers.

(i)  $\beta$ -Naphthol-1-sulphonic Acid (*Oxy-Tobias acid*, *Armstrong Acid*) is the main product, along with a small proportion of the 8-sulphonic acid, of the sulphonation of  $\beta$ -naphthol with 90% sulphuric acid at 35–45°, or at lower temperatures (see Nat. Aniline and Chemical Co., U.S.P. 1913748). It is isolated, after neutralisation with lime and separation of the gypsum, by salting out or precipitation as the sparingly soluble basic barium salt (Tobias, G.P. 74688). It is manufactured by the action of sulphur trioxide below 16°, or of chlorosulphonic acid below 10°, on  $\beta$ -naphthol suspended in an inert liquid, such as *o*-nitrotoluene (Du Pont, U.S.P. 1662396; 1716082).

*Identification.*—Both basic and normal salts, except the basic barium salt, are easily soluble in water. The normal barium salt,



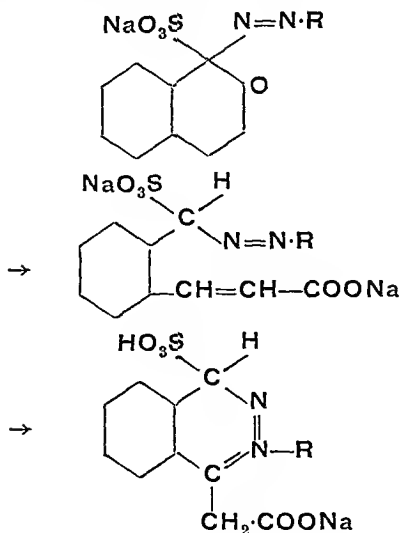
potassium salt, KA, and sodium salt, NaA, crystallise from alcohol in scales; the disodium salt,  $\text{Na}_2\text{A} + 2\text{C}_2\text{H}_5\text{OH}$ , in scales, shows no fluorescence in aqueous solution. Neutral solu-

tions of the salts give an indigo-blue coloration with ferric chloride; acid solutions hydrolyse to  $\beta$ -naphthol on heating.

*Reactions.*—With sulphuric acid at 50–60°,  $\beta$ -naphthol-6:8-disulphonic acid is formed. Heated with 20% ammonia at 220–230°, it yields  $\beta$ -naphthylamine-1-sulphonic acid. The latter may also be prepared by the bisulphite reaction, but the product obtained by saturating the disodium salt with sulphur dioxide is not a sulphurous ester of the Bucherer type (Voroshchov and Kasatkin, Ber. 1929, 62 [B], 57).

With diazotised bases in concentrated alkaline solution, coupling occurs in the 1-position, the sulphonic acid group being eliminated. Coupled in neutral or faintly alkaline solution, intermediate products are formed with certain diazotised bases, such as *p*-nitrodiazobenzene. These were formerly regarded as diazo-oxides (Bucherer and Tama, J. pr. Chem. 1930, [ii], 127, 39), but have been shown by Rowe and his collaborators to be sodium 1-aryldiazo- $[\beta]$ -naphthaquinone-1-sulphonates. A freshly prepared alkaline solution of these intermediate products on acidification gives the azo-dye, with elimination of the sulphonic group, but certain of them (from *p*-nitrodiazobenzene, etc.), after standing in

alkaline solution, give, on acidification, complex phthalazine derivatives.



For this reaction it is essential that a free hydroxyl group shall occupy the 2-position; if replaced by amino-, methoxy-, or bromo-, no reaction occurs (J.C.S. 1926, 690; 1928, 2550, 2556; 1931, 1073; 1932, 11, 473, 1118; 1935, 1253, 1796; 1936, 1098, 1704; 1937, 90).

$\beta$ -Naphthol-1-sulphonyl chloride, m.p. 124°, has been obtained by deacetylation of the acetyl derivative (Anschütz and Maxim, Annalen, 1918, 415, 89).

**Estimation.**— $\beta$ -Naphthol-1-sulphonic acid may be estimated by bromopotentiometric titration (Harland, Forrester, and Bain, J.S.C.I. 1931, 50, 100r).

(ii)  $\beta$ -Naphthol-3-sulphonic Acid has been prepared from 2-methoxy-3-naphthoamide by conversion into 2-methoxy-3-aminonaphthalene and thence, through the sulphinic acid and the sulphonic acid, to the 2-methoxynaphthalene-3-sulphonic acid which is readily demethylated (Holt and Mason, J.C.S. 1931, 378).

**Identification.**—The feebly alkaline solution shows a blue fluorescence, and the acid and its salts give a blue colour with ferric chloride. The sodium salt,  $\text{NaA} + \text{H}_2\text{O}$ , crystallises in plates; the aniline salt melts at 241–242°. The amide, yellow, melts at 110°.

**Reactions.**—It couples with diazotised bases to form dyes giving deeper shades than those from the 6-sulphonic acid.

(iii)  $\beta$ -Naphthol-4-sulphonic Acid may be obtained from  $\beta$ -naphthylamine-4:8-disulphonic acid by hydrolysis with water or 10% sulphuric acid under pressure at 170–185° (Kalle, G.P. 78603). It may also be obtained from diazotised 1-amino-2-naphthol-4-sulphonic acid by reduction with glucose, or with sodium sulphide (Masschalk, Bull. Soc. chim. 1929, [iv], 45, 651), or by boiling with absolute alcohol (Morgan and Jones, J.S.C.I. 1923, 42, 97r), or from 2-naphthol-1:4-disulphonic acid (Krebs and Vannotti, Helv. Chim. Acta, 1938, 21, 1228).

**Reactions.**—Heated with ammonia under pressure it gives  $\beta$ -naphthylamine-4-sulphonic acid. Digested with 60% caustic soda at 230–

280° it yields *o*-toluic acid (Kalle, G.P. 79028). When the *o*-acyl derivatives are nitrated, a mixture of 6- and 7-nitro-compounds is formed (Geigy, B.P. 553535, 1941). The 6-nitro derivative is described by Ruggli (Helv. Chim. Acta, 1929, 12, 1042). It couples with diazotised bases (I.G., B.P. 292344).

(iv)  $\beta$ -Naphthol-5-sulphonic Acid has been prepared from  $\beta$ -naphthylamine-5-sulphonic acid by the diazo-reaction (Dahl, B.P. 7712, 1884; Claus, J. pr. Chem. 1889, [ii], 49, 315). It forms azo-dyes which are not commercially important. Fused with caustic soda it gives 1:6-dihydroxynaphthalene.

(v)  $\beta$ -Naphthol-6-sulphonic Acid (*Schäffer Acid*) is obtained as main product of the sulphonation of  $\beta$ -naphthol with sulphuric acid at 100° (Armstrong, Ber. 1882, 15, 201). It is the chief product of sulphonation of  $\beta\beta'$ -dinaphthyl ether at 90–100° (Brönnner, B.P. 3606, 1883). It has also been obtained by fusion of sodium naphthalene-2:6-disulphonate with caustic alkali, or from  $\beta$ -naphthylamine-6-sulphonic acid by the bisulphite method (Badische, G.P. 134401).

**Preparation.**— $\beta$ -Naphthol (1 mol.) is stirred with monohydrate (2 mol.) at 100° until sulphonation is complete. The product is drowned in water, the solution neutralised with lime, filtered from gypsum, converted into the sodium salt with sodium carbonate, filtered from calcium carbonate and the filtrate salted to 20% with common salt, after concentration if necessary. The sodium salt of  $\beta$ -naphthol-6-sulphonic acid is precipitated leaving 3:6-disulphonate (R-salt) in solution. If the sulphonation is carried out at a lower temperature, or with less acid, the by-product left in solution is chiefly  $\beta$ -naphthol-8-sulphonate (Fierz-David, Farbenchemie, 1938; see Vorontzow, J. Chem. Ind. Russ., 1930, 7, 1287; B. 1932, 138).

**Identification.**—The acid forms easily soluble, non-deliquescent scales with  $\text{H}_2\text{O}$ , m.p. 125°. The anhydrous acid has m.p. 167° (Engel and Hutchinson, J. Amer. Chem. Soc. 1930, 52, 211). Most of the salts of this acid crystallise in plates.

Salt.	Water of crystallisation, mol.	Solubility, g. salt in 100 c.c. solution at 20°.
NaA . .	2	about 1.7
MgA <sub>2</sub> . .	8	0.96
BaA <sub>2</sub> . .	6	1.74
ZnA <sub>2</sub> . .	8	0.87
MnA <sub>2</sub> . .	8	1.20
CoA <sub>2</sub> . .	8	0.50
NiA <sub>2</sub> . .	8	0.53
PbA <sub>2</sub> . .	6	1.81

(Ephraim and Pfister, Helv. Chim. Acta, 1925, 8, 229).

In aqueous solution the salts show a blue fluorescence and give a pale green coloration with ferric chloride. With nitric acid, solutions of the salts become carmine-red owing to the formation of an indophenol derivative of [ $\beta$ ]-naphthaquinone, which has been isolated (Nietzki and Knapp, Ber. 1897, 30, 187).

**Reactions.**—With diazotised bases azo-dyes



are formed. With nitrous acid 1-nitroso- $\beta$ -naphthol-6-sulphonic acid is formed which, with ferric chloride, gives a valuable *Naphthol Green*. With nitric acid in presence of sulphuric acid some 1-nitro derivative is formed, but the main product is a dinitro derivative. On sulphonation with monohydrate,  $\beta$ -naphthol-3:6-disulphonic acid is formed. By the bisulphite reaction, or by heating with ammonia alone under pressure,  $\beta$ -naphthylamine-6-sulphonic acid may be prepared. Fused with caustic soda 2:6-dihydroxy-naphthalene is obtained. By oxidation with aqueous ferric chloride, 2:2'-dihydroxy-1:1'-dinaphthyl-6:6'-disulphonic acid is formed (Joffe, J. Gen. Chem. Russ. 1935, 5, 877, 950; A. 1936, 67).

**Derivatives.**—The *phenyl ester*, needles, m.p. 131°; *amide*, scales, m.p. 237–239°; *dimethylamide*, scales, m.p. 125°; and *anilide*, needles, m.p. 161°, have been obtained from the corresponding derivatives of 1-carboxy- $\beta$ -naphthol-6-sulphonyl chloride by elimination of carbon dioxide (Bayer, G.P. 278091).

(vi)  $\beta$ -Naphthol-7-sulphonic Acid (*F-acid*) is a product, along with the 6-sulphonic acid, of sulphonation of  $\beta$ -naphthol with monohydrate at 100–130° but this is not a method for its manufacture. It can be obtained from  $\beta$ -naphthylamine-7-sulphonic acid by the bisulphite method (Buecherer, J. pr. Chem. 1904, [ii], 69, 73).

**Preparation.**—Sodium naphthalene-2:7-disulphonate is digested with four times its weight of 50% caustic soda solution under pressure at 225° for 10 hours. From the solution of the melt in twice its weight of water, after it has been acidified and boiled to remove sulphur dioxide, sodium  $\beta$ -naphthol-7-sulphonate crystallises in the cold (Cassella, G.P. 42112; B.P. 12908, 1886). If a crude mixture of sodium naphthalene-2:6- and 2:7-disulphonate is used for this preparation, the 6-sulphonate may be removed by salting out its less soluble sodium salt from alkaline or acid solution (Cassella, G.P. 45221).

**Identification.**—The acid forms hydrated needles, m.p. 89°, readily soluble in water or alcohol; the *barium* salt sparingly soluble prisms, the *magnesium* salt,  $MgA_2 + 5\frac{1}{2}H_2O$ , scales; the *potassium* salt,  $KA + H_2O$ , readily soluble rhombs; the *sodium* salt,  $NaA + 2\frac{1}{2}H_2O$ , large scales soluble in 12.5 parts of water at 15°. In alkaline solution the salts show a pure blue fluorescence, and in neutral solution give a dark blue coloration with ferric chloride.

**Reactions.**—It couples with diazotised bases forming azo-dyes. With nitrous acid it gives 1-nitroso- $\beta$ -naphthol-7-sulphonic acid, convertible into a *Naphthol Green* by iron salts (Cassella, l.c.). On sulphonation with chlorosulphonic acid it yields  $\beta$ -naphthol-1:7-disulphonic acid, but with sulphuric acid at 120°, the 3:7-disulphonic acid. By the bisulphite method, or heated with 20% ammonia at 250°, it is converted into  $\beta$ -naphthylamine-7-sulphonic acid; with dimethylamine at 220°, the product is dimethyl- $\beta$ -naphthylamine-7-sulphonic acid. Fused with caustic soda it yields 2:7-dihydroxynaphthalene.

(vii)  $\beta$ -Naphthol-8-sulphonic Acid (*Croceine Acid*) may be obtained pure from  $\beta$ -

naphthylamine-8-sulphonic acid by the bisulphite reaction (Badische, G.P. 134401).

**Preparation.**— $\beta$ -Naphthol is stirred as rapidly as possible into twice its weight of sulphuric acid, at 50° until dissolved in about 15 minutes (Bayer, G.P. 18027; 20397), or at a temperature not exceeding 20° over several days (Leonhardt, G.P. 33857). It is separated from the 6-sulphonic acid, produced at the same time, by neutralisation with calcium hydroxide, filtering hot from gypsum and concentrating the filtrate until the 6-sulphonate crystallises out, whereby 80% of the 6-sulphonate is removed. The remainder may be removed, after conversion to the sodium salt, either by coupling with the requisite amount of diazotised base and salting out the dye, or, in the laboratory, by extraction of the dried salt with 90% alcohol, in which the 8-sulphonate alone is appreciably soluble. The product is obtained as a solution in either case.

**Identification.**—The acid is hydrolysed in hot aqueous solution giving  $\beta$ -naphthol. It forms both normal and basic salts which are much more soluble than the salts of the 6-sulphonic acid. The *sodium* salt forms six-sided scales, the *basic disodium* salt,  $Na_2A + 2C_2H_5OH$ , deliquescent needles from 95% alcohol, in which it dissolves very easily at the boiling-point, but only sparingly (1 in 100) at 15°; the *lead* salt,  $PbA_2 + 2\frac{1}{2}H_2O$ , forms rhombohedra. Unlike its isomers it does not give a nitroso-compound.

**Reactions.**—It couples with diazotised bases, but only very slowly, forming valuable azo-dyes. Warmed with dilute nitric acid it yields 1:6-dinitro- $\beta$ -naphthol-8-sulphonic acid. On sulphonation with sulphuric acid below 50°, it gives  $\beta$ -naphthol-6:8-disulphonic acid. By the bisulphite method, or when heated with ammonia under pressure, it yields  $\beta$ -naphthylamine-8-sulphonic acid. Fused with caustic soda it yields 1:7-dihydroxynaphthalene.

#### $\beta$ -NAPHTHOLDISULPHONIC ACIDS.

The technically important  $\beta$ -naphtholdisulphonic acids are the 3:6-(*R-acid*) and 6:8-(*G-acid*) isomers.

(i)  $\beta$ -Naphthol-1:4-disulphonic Acid is described (Geigy, B.P. 485971) as being formed by heating an aqueous solution or suspension of 1:2-aminonaphthol-4-sulphonic acid with sodium sulphite in presence of copper, zinc, aluminium or their salts. The reaction is general with 1:2-aminonaphtholsulphonic acids. It is also formed in high yield, when sodium 1-diazo-2-naphthol-4-sulphonate in aqueous solution interacts with 1 mol. of sodium sulphite and the resulting orange solution is heated (Kreiser and Vannotti, *Helv. Chim. Acta*, 1938, 21, 1222). The *disodium* salt,  $3H_2O$ , forms thin needles; *dipotassium* salt six-sided prisms. The 1-sulphonic group is readily removed by hydrolysis. The 6-nitro-compound is known (*ibid.*).

(ii)  $\beta$ -Naphthol-1:5-disulphonic Acid (*sulphonyl chloride*, m.p. 177°) is formed by the interaction of chlorosulphonic acid and  $\beta$ -naphthol-5-sulphonic acid (Pollak, Gebauer-Fülnegg *et al.*, *Monatsh.* 1929, 53–54, 83).

(iii)  $\beta$ -Naphthol-1:6-disulphonic Acid is obtained in 90% yield by sulphonation of  $\beta$ -



naphthol-6-sulphonic acid with 40% oleum at 25°; at higher temperatures the 2:6- and 6:8-disulphonic acids predominate (Schtscherbatschev, J. Appl. Chem. Russ. 1935, 8, 1216; B. 1936, 181); also from naphthalene-1:2-diazo-oxide-6-sulphonic acid (Krebsner and Vanotti, l.c.); the ethyl ether has been obtained by sulphonating  $\beta$ -ethoxynaphthalene or its 6-sulphonyl chloride in chloroform solution with chlorosulphonic acid (Lapworth, Proc. C.S. 1895, 11, 51).

**Identification.**—The normal potassium salt,  $K_2A + H_2O$ , crystallises in slender prisms; the sodium salt,  $Na_2A + 3H_2O$ , in elongated flakes (Engel, J. Amer. Chem. Soc. 1930, 52, 2835).

(iv)  $\beta$ -Naphthol-1:7-disulphonic Acid obtained, either from sodium  $\beta$ -naphthol-7-sulphonate by sulphonation in the cold with chlorosulphonic acid (Dressel and Kothe, Ber. 1894, 27, 1206), or from  $\beta$ -naphthylamine-1:7-disulphonic acid by the diazo-reaction.

**Identification.**—The barium salt forms sparingly soluble needles; the potassium salt,  $K_2A + 1\frac{1}{2}H_2O$ , moderately soluble prisms; the sodium salt, very soluble needles. In alkaline solution the salts give a pale blue fluorescence. It does not couple with diazotised bases.

**Reactions.**—Boiled with 10% hydrochloric acid, it is hydrolysed to  $\beta$ -naphthol-7-sulphonic acid. Digested with 25% ammonia at 180–200°, or by the bisulphite reaction, it yields  $\beta$ -naphthylamine-1:7-disulphonic acid.

(v)  $\beta$ -Naphthol-3:6-disulphonic Acid (R-acid) is a product of sulphonation of  $\beta$ -naphthol with three to four times its weight of sulphuric acid, the amount formed depending on the temperature and duration of the treatment (cf. Vorontzov and Sokolova, Anilinokras. Prom. 1935, 5, 334; B. 1936, 440).

**Preparation.**—Finely powdered  $\beta$ -naphthol is stirred with four times its weight of sulphuric acid, without cooling, and the product heated at 120°, with continuous stirring, until a sample, on addition of sodium nitrite in excess, no longer gives a red coloration (Beyer and Kegel, G.P. 33916; B.P. 7097, 1884). The R-acid is separated, as sodium salt, by pouring the sulphonation mass into brine, the 6:8-disulphonic acid, formed as by-product, remains in solution (Nat. Aniline and Chemical Co., U.S.P. 1880442). Alternatively, the solution in water is neutralised with lime and the sparingly soluble sodium-calcium salt precipitated by addition of caustic soda (Calco. Chemical Co. Inc., U.S.P. 1701259). Selective crystallisation from aqueous alcohol has also been used for the separation of the 3:6- from the 6:8-disulphonic acid (Kawaguchi, J. Chem. Ind. Japan, 1923, 6, 1233; B. 1924, 504).

**Identification.**—The acid forms silky, deliquescent needles, very soluble in water or alcohol; the barium salt,  $BaA + 6H_2O$ , needles, soluble in 12 parts boiling water, but insoluble in alcohol; the sodium salt, aggregates of minute needles readily soluble in cold water, but only sparingly soluble in alcohol or brine. In aqueous solution the salts show a bluish-green fluorescence. The readily soluble aluminium salt has been used as an antiseptic and astringent, "Alumnol."

**Reactions.**—It couples readily with diazotised

bases and is an important component of azo-dyes. With nitrous acid the 1-nitroso derivative is formed. On sulphonation with 20% oleum it gives  $\beta$ -naphthol-3:6:8-trisulphonic acid. With sodium sulphite in presence of manganese peroxide, it forms  $\beta$ -naphthol-1:3:6-trisulphonic acid. It is not readily hydrolysed, but with 20% sulphuric acid at high temperature it gives  $\beta$ -naphthol-6-sulphonic acid (Friedländer and Lucht, Ber. 1893, 26, 3029).

By the bisulphite reaction, or when heated with ammonia under pressure, it yields  $\beta$ -naphthylamine-3:6-disulphonic acid. Fused with caustic soda at 220–240°, it gives 2:3-dihydroxynaphthalene-6-sulphonic acid. It is readily monobrominated by bromine water and this reaction may be used as the basis of a method of estimation in presence of the 6:8-disulphonic acid (Forrester and Bain, J.S.C.I. 1930, 49, 410r). Condensed with Michler's hydrol followed by oxidation it forms a valuable green acid wool dye.

(vi)  $\beta$ -Naphthol-3:7-disulphonic Acid is formed when sodium  $\beta$ -naphthol-7-sulphonate (1 part) is heated with sulphuric acid (2 parts) at 120° for about 12 hours, or with 3–4 parts of the acid on a water bath (Dressel and Kothe, Ber. 1894, 27, 1206). It can also be obtained by partial hydrolysis of  $\beta$ -naphthol-1:3:7-trisulphonic acid with 10% hydrochloric acid.

**Identification.**—The normal barium salt,  $BaA + 2\frac{1}{2}H_2O$ , forms small prisms soluble in 185 parts boiling water; the sodium salt,  $Na_2A$ , is soluble in 100 parts of 80% alcohol and very soluble in water, the solution showing green fluorescence (Weinberg, *ibid.* 1887, 20, 2911).

**Reactions.**—It couples with diazotised bases forming azo-dyes. On sulphonation with 25% oleum at 80–90° it yields  $\beta$ -naphthol-1:3:7-trisulphonic acid. With 20% sulphuric acid at a high temperature it is hydrolysed to  $\beta$ -naphthol-7-sulphonic acid. By the bisulphite reaction or with 25% ammonia at 200° it yields  $\beta$ -naphthylamine-3:7-disulphonic acid. Fused with caustic soda it yields 2:7-dihydroxynaphthalene-3-sulphonic acid.

(vii)  $\beta$ -Naphthol-4:7-disulphonic Acid has been prepared by boiling diazotised  $\beta$ -naphthylamine-4:7-disulphonic acid with water. Heated with aniline and aniline hydrochloride at 150–170° it yields 1:3-dianilinonaphthalene-6-sulphonic acid (Bayer, G.P. 77866; B.P. 16780, 1893).

(viii)  $\beta$ -Naphthol-4:8-disulphonic Acid has been obtained from  $\beta$ -naphthylamine-4:8-disulphonic acid by the diazo-reaction. The calcium salt forms prisms. A solution of the sodium salt shows a blue fluorescence.

**Reactions.**—In concentrated solution it couples with diazotised bases to form azo-dyes. On desulphonation with zinc dust and boiling dilute caustic soda, it yields both  $\beta$ -naphthol-4- and -8-sulphonic acids (Kalle, G.P. 233934). Digested with aniline and aniline hydrochloride at 150–170°, it yields 1:3-dianilinonaphthalene-5-sulphonic acid.

(ix)  $\beta$ -Naphthol-5:7-disulphonic Acid is reported to have been prepared from the corresponding  $\beta$ -naphthylamine-5:7-disulphonic acid by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii], 70, 347).

(x)  $\beta$ -Naphthol-6:8-disulphonic Acid (G-acid) has been prepared from  $\beta$ -naphthylamine-6:8-disulphonic acid by the diazo-reaction, or by sulphonation of  $\beta$ -naphthol-8-sulphonic acid. It is also a product of sulphonation of  $\beta$ -naphthol at a moderate temperature.

**Preparation.**—Finely powdered  $\beta$ -naphthol is added slowly to three times its weight of monohydrate, while the temperature is kept below  $35^\circ$  by cooling. The mixture is stirred at  $35^\circ$  for some hours until a test shows complete solubility in water. It is then poured into a relatively small quantity of water, converted to the calcium salt, using lime, and thence to the potassium salt, which crystallises in presence of mineral acid from the more soluble R-salt. The yield is about 55% of the theoretical. The R-salt may also be separated by selective coupling with a diazo-compound and salting out as the azo-dye; the G-acid remains in solution (see Vorontzov and Sokolova, Anilinokras. Prom. 1935, 5, 334; B. 1936, 440 for the conditions of sulphonation, and Masters, B.P. 210120 for method of isolation).

**Identification.**—With the notable exception of the potassium salt which dissolves in 2.3 parts boiling water and is of relatively low solubility in cold water, and of the ammonium salt, the salts of pure G-acid are much more soluble in water than the corresponding salts of R or Schäffer acids.

**Reactions.**—It couples only slowly and in concentrated solution with diazotised bases, but it forms valuable azo-dyes. Sulphonated with 20% oleum it yields  $\beta$ -naphthol-3:6:8-trisulphonic acid. It is not readily hydrolysed by boiling dilute mineral acids, but at higher temperatures, or with sodium amalgam in the cold, it gives  $\beta$ -naphthol-6-sulphonic acid. By the bisulphite method, or with ammonia under pressure, it gives  $\beta$ -naphthylamine-6:8-disulphonic acid. Fused with caustic soda at  $200$ – $230^\circ$  it gives 1:7-dihydroxynaphthalene-3-sulphonic acid; and at  $260$ – $320^\circ$ , hydroxytoluic acid (Höchst, G.P. 81333). It is not so readily brominated as R-acid (Forrester and Bain, J.S.C.I. 1930, 49, 410r).

#### $\beta$ -NAPHTHOLTRISULPHONIC ACIDS.

(i)  $\beta$ -Naphthol-1:3:7-trisulphonic Acid is prepared by sulphonating either  $\beta$ -naphthol-7-sulphonic acid or  $\beta$ -naphthol-3:7-disulphonic acid with 25% oleum at  $80$ – $90^\circ$  (Dressel and Kothe, Ber. 1894, 27, 1207).

**Identification.**—The barium salt is easily soluble; the sodium salt,  $\text{Na}_3\text{A}$ , is very soluble in water, but only sparingly so in alcohol, gives with ferric chloride a violet coloration and, in alkaline solution, shows a bluish-green fluorescence. It does not couple with diazotised bases.

**Reactions.**—By sulphonation with 40% oleum at  $120$ – $130^\circ$  it is converted into  $\beta$ -naphthol-1:3:6:7-tetrasulphonic acid. Boiled with 10% mineral acid it is hydrolysed to  $\beta$ -naphthol-3:7-disulphonic acid. Digested with 25% ammonia at  $190^\circ$  it gives  $\beta$ -naphthylamine-1:3:7-trisulphonic acid.

(ii)  $\beta$ -Naphthol-3:5:7-trisulphonic Acid has been obtained from  $\beta$ -naphthylamine-3:5:7-trisulphonic acid by the diazo-reaction. It

couples with diazotised bases forming azo-dyes (Dressel and Kothe, l.c.).

(iii)  $\beta$ -Naphthol-3:6:7-trisulphonic Acid has been prepared from  $\beta$ -naphthol-1:3:6:7-tetrasulphonic acid by hydrolysis with water or dilute mineral acid; and from  $\beta$ -naphthylamine-3:6:7-trisulphonic acid by the diazo-reaction (Dressel and Kothe, *ibid.* 1894, 27, 1209).

**Identification.**—The barium salt is gelatinous; the sodium salt,  $\text{Na}_3\text{A}$ , needles, is less soluble than its isomers in water, brine, or alcohol, gives a violet coloration with ferric chloride, and shows, in alkaline solution, a bluish-green fluorescence.

**Reactions.**—It couples, in alkaline solution, with diazotised bases forming azo-dyes. In neutral or acid solution it forms salts with tetra-azo derivatives of the diphenyl series (Bayer, G.P. 92169; B.P. 8995, 1895). Heated with 26% ammonia, it yields  $\beta$ -naphthylamine-3:6:7-trisulphonic acid. It is not hydrolysed by dilute acids. Fused with 66% caustic soda at  $220$ – $300^\circ$ , it yields the 2:7-dihydroxynaphthalene-3:6-disulphonic acid.

(iv)  $\beta$ -Naphthol-3:6:8-trisulphonic Acid is prepared by sulphonation of  $\beta$ -naphthol. Nietzki (Chem.-Ztg. 1891, 15, 296) heated  $\beta$ -naphthol with 40% oleum at  $90$ – $120^\circ$ . If the sulphonation mass is poured on to three times its weight of ice, a crystalline powder, probably the 2:3-anhydride or sultone, is precipitated, which in solution shows no fluorescence and gives no colour with ferric chloride. With alkalis, it yields the trisulphonate and this gives a violet coloration with ferric chloride and a yellowish-green fluorescence in alkaline solution. Levinstein (B.P. 706, 1883) stirred  $\beta$ -naphthol into three times its weight of monohydrate, added an equal weight of 40% oleum at  $125^\circ$  for 2 hours, and then treated with brine to separate the sodium salt.  $\beta$ -Naphthol-6-, or 8-mono-, or 3:6- or 6:8-di-sulphonic acids may be used in place of  $\beta$ -naphthol (Levinstein, Ber. 1883, 16, 462). The actual amount of the 3:6:8-trisulphonic acid formed probably depends on the time of sulphonation, rising at  $130^\circ$  to a maximum of 50–60% of that calculated (Vorontzov and Sokolova, Prom. Org. Chim. 1937, 3, 289; B. 1937, 1018).

**Reactions.**—It couples with diazotised bases forming azo-dyes. It can be desulphonated by sodium amalgam in the cold giving  $\beta$ -naphthol-6:8-disulphonic acid (Bayer, G.P. 255724; B.P. 28172, 1911). Heated with ammonia at  $200$ – $250^\circ$  it yields  $\beta$ -naphthylamine-3:6:8-trisulphonic acid. Fused with caustic soda at  $220$ – $230^\circ$  it gives a mixture of 1:7-dihydroxynaphthalene-3:6- and 2:3-dihydroxynaphthalene-6:8-disulphonic acids.

#### $\beta$ -NAPHTHOLTETRASULPHONIC ACID.

$\beta$ -Naphthol-1:3:6:7-tetrasulphonic Acid is obtained by the sulphonation of  $\beta$ -naphthol-7-sulphonic, or 3:7-disulphonic, or 1:3:7-trisulphonic acid with 40% oleum at  $120$ – $130^\circ$ , but the product undergoes desulphonation unless care is taken to prevent the solution of the mass in water, while still acid, from becoming hot (Bayer, B.P. 17141, 1893; Dressel and Kothe, Ber. 1894, 27, 1208).

**Identification.**—The barium salt is a very sparingly soluble, sandy powder; the sodium salt,  $\text{Na}_2\text{A}$ , is easily soluble in water, but insoluble in alcohol, and in alkaline solution shows a bluish-green fluorescence. It does not complex with diazotised bases.

**Reactions.**—Digested with 25% ammonia solution at  $180^\circ$ , it gives  $\beta$ -naphthylamine-1:3:6:7-tetrasulphonic acid. Boiled with dilute mineral acids it yields  $\beta$ -naphthol-3:6:7-trisulphonic acid.

#### HALOGENO- $\beta$ -NAPHTHOLS.

The course of the halogenation of  $\beta$ -naphthol presents some interesting features, in that the reaction is not simply one of substitution in the nucleus but is accompanied by the formation of derivatives of naphthoquinone and additive compounds; further, there are important differences between the courses of chlorination and bromination. The action of chlorine in acetic acid, or of hypochlorite in aqueous alkaline solution, on  $\beta$ -naphthol gives 1-chloro- $\beta$ -naphthol. Further action of chlorine in acetic acid-sodium acetate solution gives 1:1-dichloro-2-keto-1:2-dihydronaphthalene yellow, m.p.  $54^\circ$ , which is readily reduced to 1-chloro- $\beta$ -naphthol and is converted by hydrochloric acid into 1:4-dichloro- $\beta$ -naphthol. Further action of chlorine gives, by addition of chlorine, 1:1:3:4-tetrachloro-2-keto-1:2:3:4-tetrahydronaphthalene, m.p.  $102-103^\circ$  (hydrate, m.p.  $90-91^\circ$ ) from which 1:3-dichloro- $\beta$ -naphthol can be prepared. 1:4-Dichloro- $\beta$ -naphthol is reduced with some difficulty to 4-chloro- $\beta$ -naphthol (cf. Zincke, *ibid.* 1888, 21, 3387, 3552; Armstrong and Rossiter, *Proc. C.S.* 1891, 7, 32; Fries and Schimmelschmidt, *Annalen*, 1930, 484, 295).

The bromination of  $\beta$ -naphthol was studied by Armstrong and Rossiter (*Proc. C.S.* 1889, 5, 71; 1891, 7, 33, 87), Franzen and Stäuble (*J. pr. Chem.* 1921, [ii], 103, 369), Fries and Engel (*Annalen*, 1924, 439, 232) and Fries and Schimmelschmidt (*l.c.*). The first product of bromination, e.g., in acetic acid, is 1-bromo- $\beta$ -naphthol, m.p.  $82-83^\circ$ , followed by 1:6-dibromo- $\beta$ -naphthol, m.p.  $106^\circ$ , then a tri- and a tetra-bromo- $\beta$ -naphthol. The tribromo-compound was for long considered to be 1:3:6- until Fries and Schimmelschmidt (*l.c.*) advanced evidence to show that it is 1:4:6-tribromo- $\beta$ -naphthol, m.p.  $157-158^\circ$ ; the tetrabromo-compound is 1:3:4:6-tetrabromo- $\beta$ -naphthol. In all these compounds, the bromine in the 1-position is readily removed by reduction, both in acid and alkaline media (cf. I.G., B.P. 380563; 381947, 1931), and thus are prepared 6-bromo- $\beta$ -naphthol, m.p.  $129-130^\circ$ , and 4:6-dibromo- $\beta$ -naphthol, m.p.  $134-135^\circ$ . The bromination of  $\beta$ -naphthol-3-carboxylic acid follows a similar course, and 6-bromo- $\beta$ -naphthol-3-carboxylic acid has been employed for preparing 6-amino derivatives for use as azo-dye intermediates. Fries and Engel have shown that an unstable 1:1-dibromo-2-keto-1:2-dihydronaphthalene can be isolated, but this gives 1:6-dibromo- $\beta$ -naphthol on treatment with hydrobromic acid, not the 1:4-compound. Fries and Schimmelschmidt also prepared 1:3:6-tribromo- $\beta$ -naphthol, m.p.  $132^\circ$ , and 4-bromo- $\beta$ -naphthol, m.p.  $122^\circ$ .

(i) 1-Chloro- $\beta$ -naphthol is obtained by

chlorinating  $\beta$ -naphthol in acetic acid solution (Cleve, *Ber.* 1888, 21, 895; Fries and Schimmelschmidt, *l.c.*); or, better, by action of hypochlorous acid in molecular proportion on  $\beta$ -naphthol in alkaline solution (Kalle, G.P. 168824). It is also a by-product of the action of ferric chloride on  $\beta$ -naphthol (Joffe, *Anilinkras. Prom.* 1935, 5, 325). It forms monoclinic crystals, m.p.  $70-71^\circ$ .

**Reactions.**—The halogen is reactive. It is eliminated by alkali sulphite, by diazonium compounds, or by zinc dust in presence of copper (Wahl and Lantz, *Bull. Soc. chim.* 1923, [iv], 33, 93; B.P. 182084; I.G., G.P. 431165). By interaction with amines or diamines, 1-aryl-amino- $\beta$ -naphthols are formed; thus, 1-anilino- $\beta$ -naphthol, m.p.  $153-154^\circ$ , is produced from aniline (Wahl and Lantz, *Compt. rend.* 1932, 194, 464). With silver nitrate only a poor yield of 1-nitro- $\beta$ -naphthol is obtained, but with sodium sulphide, that of di-2-hydroxy-1-naphthyl-sulphide is quantitative (Ringeissen, *ibid.* 1934, 198, 2180).

(ii) 3-Chloro- $\beta$ -naphthol has been obtained, m.p.  $93^\circ$ , by reducing 1:3-dichloro- $\beta$ -naphthol with zinc dust in alcohol solution (I.G., G.P. 431165) and, m.p.  $90^\circ$ , from the 1-diazo-oxide (Marschalk, *Bull. Soc. chim.* 1928, [iv], 43, 1363). A very different m.p.,  $63-64.5^\circ$ , is given by Jambuserwala, Holt, and Mason, who prepared it from 3-amino-2-naphthyl methyl ether via 3-chloro-2-naphthyl methyl ether, m.p.  $78.5^\circ$  (*J.C.S.* 1931, 374). According to Marschalk (*Bull. Soc. chim.* 1929, [iv], 45 651), when heated with dilute sodium sulphite it gives  $\beta$ -naphthol and  $\beta$ -naphthol-4-sulphonic acid.

(iii) 4-Chloro- $\beta$ -naphthol has been obtained by reducing 1:4-dichloro- $\beta$ -naphthol (*supra*) and by Hodgson and Birtwell (*J.C.S.* 1943, 468) from 4-chloronaphthalene-1:2-diazo-oxide. It has m.p.  $100^\circ$  (methyl ether, m.p.  $44-45^\circ$ ) and its sodium salt is sparingly soluble in dilute aqueous sodium hydroxide. Its coupling with diazo-compounds has been described (I.G., G.P. 459989).

(iv) 5-Chloro- $\beta$ -naphthol has m.p.  $128^\circ$  (Claus, *J. pr. Chem.* 1889, [ii], 39, 317).

(v) 6-Chloro- $\beta$ -naphthol, m.p.  $115^\circ$ , was obtained by Ruggli *et al.* (*Helv. Chim. Acta*, 1929, 12, 1048) from 6-amino- $\beta$ -naphthol-4-sulphonic acid. It is best obtained pure by crystallisation from water. The *m-nitrobenzoate* has m.p.  $146-147^\circ$ . It has also been obtained by reducing 1:6-dichloro- $\beta$ -naphthol (I.G., G.P. 431165).

(vi) 7-Chloro- $\beta$ -naphthol, m.p.  $126.5^\circ$  (*acetate*, m.p.  $104.5^\circ$ ) has been prepared from 7-hydrazino- $\beta$ -naphthol (Franzen and Deibel, *J. pr. Chem.* 1908, [ii], 78, 154).

(vii) 8-Chloro- $\beta$ -naphthol has m.p.  $101^\circ$  (*m-nitrobenzoate*, m.p.  $176^\circ$ ) (Ruggli *et al.*, *l.c.*).

(viii) 1:3-Dichloro- $\beta$ -naphthol has been obtained by reduction of 1:1:3-trichloro-2-keto-1:2-dihydronaphthalene with stannous chloride (Zincke, *Ber.* 1888, 21, 3544). It forms needles, m.p.  $81^\circ$ . Its *acetyl* derivative has m.p.  $79-80^\circ$ . Heated with dilute potassium sulphite solution under pressure it yields 3-chloro- $\beta$ -naphthol-1-sulphonic acid; but with 10% solution at  $170^\circ$  it yields  $\beta$ -naphthol-1- and 4-sulphonic acids and

a little  $\beta$ -naphthol (Marschalk, Bull. Soc. chim. 1929, [iv], 45, 651).

(ix) 1:4-Dichloro- $\beta$ -naphthol, m.p. 123–124°, is obtained from 1:1-dichloro-2-keto-1:2-dihydronaphthalene by treatment with hydrogen chloride in acetic acid (Fries and Schimmelschmidt, *l.c.*).

(x) 1-Chloro-6-bromo- $\beta$ -naphthol, m.p. 105°, is obtained from 1:1-dichloro-2-keto-1:2-dihydronaphthalene by treatment with hydrogen bromide in acetic acid.

NITROSO- $\beta$ -NAPHTHOLS (*see Naphthaquinone-oximes*, p. 385a).

#### NITRO- $\beta$ -NAPHTHOLS.

(i) 1-Nitro- $\beta$ -naphthol is obtained, in good yield, by nitrating  $\beta$ -naphthol at 35° in presence of mercuric nitrate. It may be prepared by hydrolysis of 1-nitro-2-acet- $\beta$ -naphthalide with boiling aqueous caustic soda (Organic Syntheses, 1933, XIII, 78), or by oxidation of 1-nitroso- $\beta$ -naphthol with dilute nitric acid, or from  $\alpha$ -nitronaphthalene by heating at 50–60° with twenty times its weight of powdered caustic soda (Wohl and Aue, Ber. 1901, 34, 2444). Its *ethyl ether*, m.p. 104–105°, is obtained by action of nitrogen peroxide on  $\beta$ -naphthyl *ethyl ether*, in acetic acid. It forms yellow needles, m.p. 103°; its *sodium* salt, red needles; its *acetate*, colourless needles, m.p. 61° (Böttcher, *ibid.* 1883, 16, 1938).

(ii) 4-Nitro- $\beta$ -naphthol, obtained from 2:4-dinitro- $\alpha$ -naphthylamine by heating the derived 1-diazo-2-oxide with powdered aluminium and alcohol, forms yellow needles, m.p. 120°, is much less easily alkylated than  $\beta$ -naphthol and couples more slowly with diazotised bases (Morgan and British Dyestuffs Corp., Ltd., B.P. 152437).

(iii) 5-Nitro- $\beta$ -naphthol is prepared from 5-nitro- $\beta$ -naphthylamine by the diazo-reaction. The *m*-nitrobenzenesulphonate, m.p. 166°, is a product of nitration of  $\beta$ -naphthyl *m*-nitrobenzenesulphonate (Bell, J.C.S. 1932, 2732). It crystallises from water in yellow needles, m.p. 147°. The salts are reddish-yellow and easily soluble; the *ethyl ether* forms yellow needles, m.p. 115° (Friedländer and Szymanski, Ber. 1892, 25, 2079).

(iv) 6-Nitro- $\beta$ -naphthol has been obtained by heating 6-nitro- $\beta$ -naphthyl *ethyl ether* with a mixture of concentrated sulphuric and acetic acids. It forms yellow needles, m.p. 156–158° (Gaess, J. pr. Chem. 1892, [ii], 45, 616; 46, 160).

(v) 8-Nitro- $\beta$ -naphthol is obtained from 8-nitro- $\beta$ -naphthylamine by the diazo-reaction (Friedländer and Szymanski, *l.c.*). The *m*-nitrobenzenesulphonate, m.p. 144–146°, is a product of nitration of  $\beta$ -naphthyl *m*-nitrobenzenesulphonate (Bell, *l.c.*). It forms deep yellow needles, m.p. 144–145°. The *ethyl ether*, prepared by nitration of  $\beta$ -ethoxynaphthalene forms long golden-yellow needles, m.p. 72–73° (Gaess, *ibid.* 1891, [ii], 43, 25), and the *acetate*, needles, m.p. 101–102 (*idem*, *ibid.* 1892, [ii], 45, 615).

#### DINITRO- $\beta$ -NAPHTHOLS.

(i) 1:5-Dinitro- $\beta$ -naphthol, yellow needles, m.p. 187° (decomp.), is obtained by hydrolysis of the *m*-nitrobenzenesulphonate, which is itself a product of nitration of  $\beta$ -naphthyl *m*-nitrobenzenesulphonate with fuming nitric acid in acetic acid (Bell, J.C.S. 1933, 286).

(ii) 1:6-Dinitro- $\beta$ -naphthol is obtained by nitration of  $\beta$ -naphthol in acetic acid (Bell, *ibid.* 1932, 2732).

*Properties.*—Yellow needles, m.p. 195°; the *potassium* salt,  $KA + 2H_2O$ , sparingly soluble needles; the *ethyl ether*, yellow needles, m.p. 144°, may be obtained as a product of nitration of  $\beta$ -naphthyl *ethyl ether* at low temperature (Ryan and Keane, Sci. Proc. Roy. Dublin Soc. 1924, 17, 297). It dyes wool and silk yellow. Heated with alcoholic ammonia at 150–160° it yields 1:6-dinitro- $\beta$ -naphthylamine (Kehrmann and Matis, Ber. 1898, 31, 2419). The 8-sulphonic acid (*Croccin Yellow*) is produced by warming sodium  $\beta$ -naphthol-8-sulphonate with dilute nitric acid at 30–40° until nitration is complete (Nietzki and Zübelen, *ibid.* 1889, 22, 454). The *potassium* salt,  $KA$ , forms yellow needles, and the *basic potassium* salt,  $K_2A$ , sparingly soluble yellow needles. It dyes wool yellow but has little tinctorial power.

(iii) 1:8-Dinitro- $\beta$ -naphthol, golden scales, m.p. 195°, is obtained from the *m*-nitrobenzenesulphonate by decomposition with piperidine (Bell, J.C.S. 1933, 286).

(iv) 4:5-Dinitro- $\beta$ -naphthol, orange-red needles, m.p. 230° (approx.) is obtained similarly (Bell, *l.c.*).

#### AMINONAPHTHOLS.

All fourteen possible aminonaphthols have been prepared. The method of preparation usually affords evidence of their structure. The normal methods of preparation are:

1. Reduction of the corresponding nitro-, nitroso, or azo derivatives of  $\alpha$ - or  $\beta$ -naphthol;
2. Fusion of  $\alpha$ - or  $\beta$ -naphthylaminemonosulphonic acids with caustic alkali,  $\alpha$ -naphthylamine-4-sulphonic acid being an exception, as it gives  $\alpha$ -naphthol-4-sulphonic acid under these conditions;
3. Fusion of naphtholmonosulphonic acids with sodamide, whereby the sulphonic group is eliminated and an amino-group introduced, not necessarily in the same position.
4. Reaction of dihydroxynaphthalenes with ammonia or with ammonium sulphite and ammonia.

Of these, the sodamido reaction, although the only method for the direct conversion of naphtholmonosulphonic acids into aminonaphthols, is of limited application. The sole examples are the conversion of  $\alpha$ -naphthol-5- and 8-sulphonic acids into the corresponding aminonaphthols. But  $\alpha$ - and  $\beta$ -naphthols are themselves converted by fusion with sodamide into the corresponding 5-aminonaphthol.  $\beta$ -Naphthol-6- and -8-sulphonic acids give first  $\beta$ -naphthol and then 5-amino-2-naphthol.  $\beta$ -Naphthol-7-sulphonic acid gives both 7- and

5-amino-2-naphthol (Sachs, Ber. 1906, 39, 3010).

The aminonaphthols are amphoteric. In presence of water they are readily oxidised by air. Those with 1:2- and 1:4-substitution form naphthaquinones on oxidation with ferric chloride, chromic acid, or nitrous acid in acid solution.

The amides obtained by condensation, chiefly of 1-amino-7-naphthol, with aroyl chlorides are described as useful for pretreatment of cotton fibres which may subsequently be coloured by development with diazotised bases (Bayer, G.P. 233117; 274081; 276331; Badische, G.P. 283742; 284997; 296991; 297414; B.P. 3796, 1914; 13455, 1914; 8058, 1915).

(i) 1-Amino-2-naphthol is obtained by reduction of 1-nitroso- or 1-nitro- $\beta$ -naphthol (Zincke, Annalen, 1892, 268, 273). Sodium sulphite is the best reagent for reducing 1-nitro- $\beta$ -naphthol (Organic Syntheses, Vol. XI, p. 8). It may also be obtained from azo derivatives of  $\beta$ -naphthol, such as Orange II by reduction with sodium hydrosulphite (Grandmougin, Ber. 1906, 39, 2495) or with hydrogen under pressure at 180–200° in presence of nickel carbonate (Tetralin, G.m.b.H., G.P. 406064).

1-Arylamino-2-naphthols are obtained from 1-chloro- $\beta$ -naphthol by reaction with primary amines (Wahl and Lantz, Bull. Soc. chim. 1923, [iv], 33, 93; G.P. 365367; B.P. 182084). 1-Amino-2-methoxy- and -2-ethoxy-naphthalenes are obtained from the corresponding 1-chloro derivative by heating with ammonia in presence of copper or zinc chloride (Gesellsch., B.P. 376667).

**Properties.**—It forms scales, sparingly soluble in boiling water. The alkaline solution rapidly turns brown in air. The hydrochloride, B, HCl, forms needles (Jacobsen, Ber. 1881, 14, 806); N-acetyl derivative, scales m.p. 235° (Michel and Grandmougin, *ibid.* 1892, 25, 3433); diacetyl derivative, m.p. 116°; dibenzoyl derivative, silky needles, m.p. 235–5° (Sachs, *ibid.* 1906, 39, 3024); the ethyl ether, prisms, m.p. 51°, b.p. 300–302° (Gesellsch., *l.c.*).

**Reactions.**—It couples, in acetic acid solution, with diazotised bases forming azo-dyes. It is not diazotised by nitrous acid in presence of mineral acids, but in neutral solution, in presence of copper salts, naphthalene-1-diazo-2-oxide is formed. Ferric chloride, or other acid oxidising agent, converts it into [ $\beta$ ]-naphthaquinone. In presence of aniline, in alkaline solution, it (or its 4-sulphonic acid) is converted by action of air into 2-hydroxy-[ $\alpha$ ]-naphthaquinone-1-imine-4-anil (Wahl and Lantz, Compt. rend. 1926, 182, 976; B.P. 246482), whereas its N-phenyl derivative gives, on oxidation, [ $\beta$ ]-naphthaquinone-1-anil (*idem*, Compt. rend. 1925, 180, 1351; B.P. 191064). It forms mono- and di-ammonia additive compounds (Briner and Kuhn, Helv. Chim. Acta, 1929, 12, 106).

(ii) 1-Amino-3-naphthol is obtained by fusing  $\alpha$ -naphthylamine-3-sulphonic acid with caustic potash at 250–260° (Friedländer, Ber. 1895, 28, 1952), or from 4-nitro- $\beta$ -naphthol by reduction with tin and hydrochloric acid (Morgan and Evens, J.C.S. 1919, 115, 1133).

**Properties.**—It forms needles, decomposing

at 185°, is sparingly soluble in water and gives a violet-brown colour with ferric chloride. Its salts are easily soluble in water. The N-acetyl derivative, m.p. 179°, forms needles; the dibenzoyl derivative, m.p. 309–310°, scales (Sachs, Ber. 1906, 39, 3024).

**Reactions.**—It couples readily with diazotised bases. With nitrous acid it gives an unstable diazo-compound. Boiled with very dilute mineral acid it is slowly converted into 1:3-dihydroxynaphthalene. Heated with aqueous ammonia it gives 1:3-diaminonaphthalene. With monohydrate at room temperature it gives 1-amino-3-naphthol-4-sulphonic acid.

(iii) 1-Amino-4-naphthol may be prepared from 4-nitro- or 4-nitroso- $\alpha$ -naphthol, or from 4-azo derivatives of  $\alpha$ -naphthol by reduction with stannous chloride and hydrochloric acid (Grandmougin and Michel, Ber. 1892, 25, 976; Seidel, *ibid.* 1892, 25, 423; Russig, J. pr. Chem. 1900, [ii], 62, 30). It is also formed by elimination of carbon dioxide when 4-amino- $\alpha$ -naphthol-2-carboxylic acid is heated at 230° (Nietzki and Guitermann, Ber. 1887, 20, 1276).

**Properties.**—It forms needles, very soluble in water which, when moist, rapidly turn blue in air. Its salts are very soluble in water. The N-formyl derivative, m.p. 168°, forms rosettes (Gaess, G.P. 149022); the N-acetyl derivative, m.p. 178° (Kehrmann and Kissine, Ber. 1914, 47, 3098); the diacetyl derivative, m.p. 158°, prisms; the dibenzoyl derivative, m.p. 215°, rhombs (Sachs, *ibid.* 1906, 39, 3026); the N-dimethyl derivative, m.p. 113°, prisms; the ethyl ether, m.p. 96°, needles (Heermann, J. pr. Chem. 1892, [ii], 45, 545).

**Reactions.**—Oxidising agents, including nitrous acid, convert it into [ $\alpha$ ]-naphthaquinone. It does not couple with diazotised bases. Its hydrochloride, heated with methyl or ethyl alcohol at 170–180°, gives the monoalkyl ether of 1:4-dihydroxynaphthalene. Sulphonated with 10% oleum at 30–40°, it gives 1-amino-4-naphthol-3-sulphonic acid.

1-Acetylamino-4-naphthol is obtained by acetylation of the hydrochloride in presence of sodium acetate (Witt and Dedichen, Ber. 1896, 29, 2948), or by the action of caustic soda solution on diacetyl-1-amino-4-naphthol (Kehrmann and Kissine, *ibid.* 1914, 47, 3097). It forms needles, m.p. 187° (178°), which are moderately soluble in warm water, and couples in alkaline solution with diazotised bases to form ortho-azo-dyes. Oxidised in glacial acetic acid with sodium dichromate or nitric acid it gives di-[ $\alpha$ ]-naphthaquinone in good yield (Ullmann, Helv. Chim. Acta, 1926, 9, 442). The ethyl ether, m.p. 189°, forms needles almost insoluble in water, but soluble in 7–4 parts of boiling alcohol (Henriques, Ber. 1892, 25, 3060).

(iv) 1-Amino-5-naphthol may be obtained from  $\alpha$ -naphthylamine-5-sulphonic acid by fusion with 60% caustic soda at 240–250° (Friedländer and Lagodzinski, J.S.C.I. 1897, 16, 793); or from 1:5-diaminonaphthalene, either by digestion under pressure with dilute mineral acids, or, in 80% yield, by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii], 69, 84). It is also formed from  $\alpha$ -naphthol or from  $\alpha$ -naphthol-5-sulphonic acid by fusion with

sodamide in naphthalene at 190° or 230° respectively (Sachs, G.P. 173522; 181333; B.P. 22412, 1905; Ber. 1906, 39, 3018).

*Properties.*—It is comparatively stable in alkaline solution to air. The *hydrochloride* is crystalline; the *dibenzoyl* derivative, m.p. 276°, forms rhombic scales; the *N-dimethyl* derivative, m.p. 112°, hexagonal tables (Füssganger, *ibid.* 1892, 25, 979).

*Reactions.*—It can be diazotised, and it may be coupled, in acid or alkaline solution, with diazotised bases forming monoazo-dyes. The azo-dye obtained by coupling it with diazotised  $\alpha$ -naphthylamine-4-sulphonic acid is not red, as is the case with its isomers, but cornflower-blue in colour (Sachs, *l.c.*). Heated with 4% hydrochloric acid at 180° or by the bisulphite method, it forms 1:5-dihydroxynaphthalene; heated with bisulphite, in presence of ammonia, it gives 1:5-diaminonaphthalene. Sulphonated in the cold it gives 1-amino-5-naphthol-6-sulphonic acid but with 23% oleum at 100°, a disulphonic acid.

(v) 1-Amino-6-naphthol is formed by reduction of 5-nitro- $\beta$ -naphthol. It may be prepared in 58% yield by fusing  $\alpha$ -naphthylamine-6-sulphonic acid with caustic soda in an open vessel at 305° (Brown, Hebden, and Withrow, J. Amer. Chem. Soc. 1929, 51, 1766) or by interaction of 1-amino-6-naphthol-4-sulphonic acid with sodium amalgam. It is also formed when  $\beta$ -naphthol or its 6- or 8-sulphonic acid is heated at 230° with sodamide in naphthalene (Sachs, Ber. 1906, 39, 3016).

*Properties.*—It crystallises in scales, m.p. 190–191° (186°), shows a blue fluorescence in ammoniacal solution, rapidly darkens, when moist, in air, and with ferric chloride gives a dark blue coloration. The *N-acetyl* derivative forms needles, m.p. 215–216°; the *diacetyl* derivative, m.p. 187°; the *N-benzoyl* derivative, needles, m.p. 152°; the *dibenzoyl* derivative, needles, m.p. 223°; the *picrate*, yellow needles, m.p. 183° (Sachs, *l.c.*), 170° (Brown, Hebden, Withrow, *l.c.*). The *hydrochloride* forms dark red crystals (*idem, ibid.*).

*Reactions.*—It can be diazotised, and it couples, in acetic acid or in alkaline solution, with diazotised bases (1 or 2 mol.) forming azo-dyes.

(vi) 1-Amino-7-naphthol is obtained from 8-nitro- $\beta$ -naphthol by reduction, or from  $\alpha$ -naphthylamine-7-sulphonic acid by fusion with caustic soda in an open vessel at 305° (*idem, ibid.*).

*Properties.*—It crystallises from water in needles, m.p. 206° (Kehrmann and Engelke, *ibid.* 1909, 42, 351), gives a greenish-blue coloration with ferric chloride and, in acid or alkaline solution, shows blue fluorescence. A complete series of *N-acyl* derivatives from the formyl to the nonadecanoyl has been prepared by Fiorz-David and Kuster: the *formyl* derivative has m.p. 204°; *acetyl* m.p. 198° (decomp.); on isolated occasions samples with m.p. 167° have been obtained; *benzoyl* 211°; *diacetyl* 177°; *dibenzoyl* 208°; *ethyl ether*, m.p. 67° (Holv. Chim. Acta, 1939, 22, 97).

*Reactions.*—It can be diazotised and it couples in acetic acid or in alkaline solution with diazotised bases (1 or 2 mol.) forming azo-dyes. With sulphuric acid at 20–30° it gives 1-amino-

7-naphthol-(4)-sulphonic acid and at 100° with 20% oleum a disulphonic acid. Its methyl ether is claimed as a base suitable for coupling on the fibre with 2:3-hydroxynaphthoaryl-amides to give violet shades (I.G., B.P. 204291).

(vii) 1-Amino-8-naphthol may be prepared by fusing  $\alpha$ -naphthylamine-8-sulphonic acid with caustic alkali at 230–240° (Badische, G.P. 55404; 62289; Fichter and Gagour, Ber. 1906, 39, 3331). It may be obtained from 1:8-diaminonaphthalene by hydrolysis with dilute acid at elevated temperature, or by the bisulphite method; and from 1:8-diaminonaphthalene-4-sulphonic acid with 25% sulphuric acid at 135–140° under pressure; or from  $\alpha$ -naphthol-8-sulphonic acid by fusion with sodamide in naphthalene at 230°.

*Properties.*—It crystallises in needles, m.p. 95–97°, sparingly soluble in cold water. Its sulphate is sparingly soluble in hot water. The *N-acetyl* derivative, needles, has m.p. 168–169° and couples with diazotised bases; the *diacetyl* derivative, needles, m.p. 118–119°; *N-benzoyl* derivative, needles, m.p. 193–194°; the *N-dimethyl* derivative, hexagonal tablets, m.p. 112°.

*Reactions.*—It may be diazotised in dilute solution, but in concentrated solution, with excess of nitrite, it gives also 8-amino-[ $\beta$ ]naphthaquinoneoxime, green needles (Fichter and Gagour, *l.c.*). In alkaline solution it couples with diazotised bases forming azo-dyes. The sulphite, 1-amino-8-naphthyl sulphite (Bucherer, J. pr. Chem. 1904, [ii], 69, 61), can also be diazotised and has been used for production of azo-dyes (Badische, G.P. 211381). With 75% sulphuric acid at 130–160° it gives 1-amino-8-naphthol-7-sulphonic acid; but with sulphuric acid at 15–20° the chief product is the 5-sulphonic acid, and at 100° solely the 5:7-disulphonic acid.

(viii) 2-Amino-1-naphthol is obtained by reducing 2-nitroso- or 2-nitro- $\alpha$ -naphthol; or from [ $\beta$ ]naphthaquinonephenylhydrazono by reduction with sodium hydrosulphite (Grandmougin, Ber. 1906, 39, 2496). It may also be obtained by interaction of 2:1-diaminonaphthol-3- or 5-sulphonic acids with sodium amalgam.

*Properties.*—It crystallises in needles, sparingly soluble in cold water. Dissolved in ammonia and shaken with air it gives a green solution, on the surface of which a characteristic violet skin forms. The *N-acetyl* derivative, needles, has m.p. 128–129° and couples with diazotised bases; the *diacetyl* derivative, needles, m.p. 116°.

*Reactions.*—Nitrous acid oxidises it to [ $\beta$ ]naphthaquinone; in presence of copper salts, in neutral solution, it gives naphthalene-2-diazo-1-oxide (*see p. 274c*). Sulphonated with 10% oleum at 40–50°, it gives either the 4- or 5-sulphonic acid (Revordin and de la Harpe, *ibid.* 1893, 26, 1281).

(ix) 2-Amino-3-naphthol may be obtained from 2:3-dihydroxynaphthalene, either by heating it with 30% ammonia under pressure at 140–150°, or by the bisulphite reaction (Badische, G.P. 117471; B.P. 1387, 1900). It may also be prepared from *O*-ethers of 2-hydroxy-3-naphthoamido by treatment with hypochlorite followed by hydrolysis (I.G., B.P. 304493; 304441; 379862; *see also* Jambusorwala, Holt, and Mason, J.C.S. 1931, 373).



**Properties.**—It crystallises in needles, m.p. 234°, sparingly soluble in cold water. The *N*-benzoyl derivative has m.p. 233.5° (Sachs, l.c.); the *methyl ether*, m.p. 104–105°. Disazo-dyes are obtained by coupling it in alkaline solution with diazotised bases (Bayer, G.P. 99468). For other derivatives, cf Goldstein and Gardiol, *Helv. Chim. Acta*, 1937, 20, 516).

(x) 2-Amino-4-naphthol has been obtained by heating 1:3-dihydroxynaphthalene with ammonia under pressure at 130–140°. It forms a sparingly soluble *hydrochloride*. The *N*-phenyl derivative is rapidly oxidised in alkaline solution to 2-anilino [*a*]-naphthaquinone. The azo-dyes derived from it resemble those from 1-amino-3-naphthol (Friedländer and Rüdtt, *Ber.* 1896, 29, 1612).

(xi) 2-Amino-5-naphthol can be obtained by fusion of  $\beta$ -naphthylamine-5-sulphonic acid with caustic potash at 260–270°. It is also obtained by fusion of  $\beta$ -naphthylamine-1:5-disulphonic acid with alkali, or by heating 6-amino- $\alpha$ -naphthol-5-sulphonic acid with mineral acid (Bucherer and Wahl, *J. pr. Chem.* 1921, [ii], 103, 129).

(xii) 2-Amino-6-naphthol is obtained by reduction of 2-amino-6-naphthol-4-sulphonic acid with sodium amalgam. The *methyl ether* has been prepared from 2:6-dihydroxynaphthalene (Windaus, *Ber.* 1924, 57 [B], 1738). *N*-Arylated derivatives are obtained from *N*-arylated  $\beta$ -naphthylamine-6-sulphonic acid by fusion with alkali (I.G., B.P. 341120).

**Properties.**—It crystallises in scales, m.p. 190–195° (Jacchia, *Annalen*, 1902, 323, 127); *dibenzoyl* derivative, needles, m.p. 233.5°; *ethyl ether*, m.p. 90–91°, b.p. 330°. It couples in alkaline solution with diazotised bases forming monoazo-dyes (Bayer, G.P. 164516; B.P. 18569, 1902).

(xiii) 2-Amino-7-naphthol is formed by fusion of  $\beta$ -naphthylamine-7-sulphonic acid with 50% caustic soda at 260–300°. It may be obtained from 2:7-dihydroxynaphthalene by heating with ammonia under pressure, or by the bisulphite method (Franzen and Deibel, *J. pr. Chem.* 1908, [ii], 78, 155), or from 2:7-diamino-naphthalene by the bisulphite reaction (Badische, G.P. 134401). Mixed with 1-amino-6-naphthol, it is a product of heating  $\beta$ -naphthol-7-sulphonic acid with sodamide in naphthalene at 230° (Sachs, *Ber.* 1906, 39, 3017; B.P. 22412, 1905).

**Properties.**—It forms needles, m.p. 201°, sparingly soluble in water. The *N*-acetyl derivative has m.p. 232°; the *diacetyl* derivative, m.p. 156° (Raiford and Talbot, *J. Amer. Chem. Soc.* 1927, 49, 559); the *dibenzoyl* derivative, needles, m.p. 187.5°; the *N*-phenyl derivative, needles, m.p. 160° (Kalle, G.P. 60103).

**Reactions.**—It may be diazotised. It couples in acid or in alkaline solution with diazotised bases forming azo-dyes (Casella, G.P. 71329). 2:7-Diaminonaphthalene is formed from it by the bisulphite method. With sulphuric acid at 30° it gives 2-amino-7-naphthol-3:6-disulphonic acid. With chlorosulphonic acid in presence of pyridine it gives 2:7-aminonaphthol-*N*-sulphonic acid (I.G., B.P. 328032).

The trimethylammonium chloride, obtained by heating the aminonaphthol in alkaline alcoholic solution with methyl chloride under

pressure at 110° couples with diazotised bases forming azo-dyes (Geigy, G.P. 90310).

(xiv) 2-Amino-8-naphthol is obtained by fusion of  $\beta$ -naphthylamine-8-sulphonic acid with caustic alkali at 260–270°, or by heating 1:7-dihydroxy- $\beta$ -naphthoic acid with ammonia at 170–180° (Friedländer and Zinberg, *Ber.* 1896, 29, 40).

**Properties.**—It crystallises in scales, m.p. 158°. Its *N*-acetyl derivative, needles, has m.p. 210–211°.

**Reactions.**—It couples in acetic acid, or in alkaline solution, with diazotised bases forming azo-dyes (Bayer, G.P. 220532). The *N*-acetyl derivative on oxidation with chromic-acetic acid gives 7-acetylamino-[*a*]-naphthaquinone (I.G., B.P. 291340).

#### AMINONAPHTHOLSULPHONIC ACIDS.

Of the very large number of aminonaphtho-mono-, di-, and tri-sulphonic acids theoretically possible, many have been described, including fifty monosulphonic acids. A relatively small number only are of technical importance and this by reason of the dyestuffs prepared from them. The remainder are of little technical interest and information on their properties is scanty.

**General Methods of Preparation.**—The chief method used for production of those acids which are of technical importance is fusion of the appropriate naphthylamine-di- or tri-sulphonic acid with concentrated caustic soda, or, less generally, caustic potash solution at temperatures of the order of 180–200°. With sulphonic acids of  $\alpha$ -naphthylamine the sulphonic group in position 8 is that most easily replaced (this is reported to be assisted by conducting the fusion in presence of ammonia) (Newport Co., U.S.P. 1573056; 1670406), next that in position 5; groups in positions 2 or 4 resist displacement. With sulphonic acids from  $\beta$ -naphthylamine, the sulphonic group in position 4, 5, or 8 is easily replaced, that in position 1 or 6 resists displacement. If the temperature is too high or the alkali too weak, the amino-group also may be eliminated with formation of a dihydroxynaphthalenesulphonic acid.

Other methods used for the production of these acids are:

1. Reduction of nitroso or azo derivatives of naphtholsulphonic acids with sodium hydrosulphite or other reducing agents. By these methods the 1:2-, 1:4-, and 2:1-aminonaphtholsulphonic acids are produced.
2. Hydrolysis of one amino-group of a diaminonaphthalenesulphonic acid, either by heating with dilute mineral acids, or water under pressure, or by the bisulphite method.
3. Amination of one hydroxyl group of dihydroxynaphthalenesulphonic acids with aqueous ammonia under pressure. With  $\alpha\beta$ -dihydroxynaphthalenesulphonic acids, the hydroxyl radical in the  $\beta$ -position is the more easily exchanged for the amino-group.
4. Sulphonation of certain aminonaphthols with sulphuric acid or oleum.



The constitution of the acids is usually known from the structure of the naphthylamine- or nitro- (or azo-) naphthel-sulphonic acid used for the preparation, but confirmation can frequently be obtained by action of sodium amalgam, which eliminates  $\alpha$ -sulphonic more readily than  $\beta$ -sulphonic groups, or by action of boiling 20% hydrochloric acid which removes the sulphonic group when in the 4-position relative to hydroxyl.

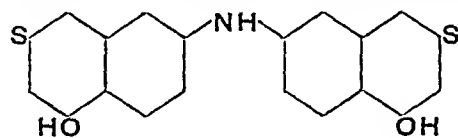
**General Properties.**—Except in respect of their properties as dyestuff intermediates, little information has been published about the properties of the acids, which are usually distinguished by the fluorescence or non-fluorescence of their alkali-salt solutions and by the colorations given with ferric chloride or bleaching-powder solutions. Nevertheless certain of these acids are important by reason of their property of forming two series of azo-dyestuffs, when coupled with diazotised bases, which are tinctorially, as well as chemically, different in character. Provided the amine- and hydroxyl-groups are in different nuclei, and the sulphonic acid group or groups so situated that the diazo-complex enters only into the *ortho*-position relatively to these radicals, coupling in weak acid solution will lead to the entry of the azo-group *ortho* to the amino-group and in alkaline solution, *ortho* to the hydroxyl group. The monoazo-compound resulting from acid coupling conditions may be capable of coupling under alkaline conditions with a second molecule of a diazo-compound. Naphthol Blue Black (Colour Index No. 246) is an example. The technically important acids of this class are Gamma acid (2-amino-8-naphthol-6-sulphonic acid), J-acid (2-amino-5-naphthol-7-sulphonic acid), S-acid (1-amino-8-naphthol-4-sulphonic acid), H-acid (1-amino-8-naphthol-3:6-disulphonic acid), and K-acid (1-amino-8-naphthol-4:6-disulphonic acid). Of the acids derived from 1-amino-8-naphthol, only these in which *ortho*-azo-dyes are obtained by coupling are of technical importance, viz.: S-, H-, and K-acids.

The monosulphonic acids derived from 1:2- and from 2:1-aminonaphthel treated with nitrous acid are oxidised in acid solution, but, in absence of free acid, they are diazotised and form *ortho*-hydroxyazo-dyes remarkable for their fastness.

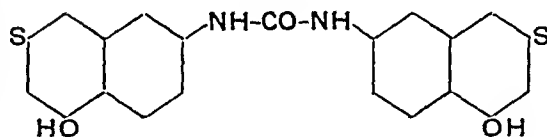
Valuable menezazo-dyes are also derived from N-substituted aminonaphthelsulphonic acids which differ in shade and degree of fastness from the comparable dyes prepared from the parent acid. Substituents may be alkyl (ethyl, etc.), acyl (acetyl or carbenyl, etc.), aryl (phenyl) and substituted aryl (nitroaryl, salicylsulphenyl, etc.).

A special interest attaches to 2-amino-5-naphthol-7-sulphonic acid (J-acid) by reason of the fact that, unlike its isomers, except 1-amino-5-naphthol-7-sulphonic acid, this acid, and its N-substituted derivatives, endow most of the azo-dyes derived from them with the valuable property of dyeing unmerdanted cotton. This property was first utilised in the introduction of dyes produced from 5:5'-dihydroxy-2:2'-dinaphthylamine-7:7'-disulphonic acid (I) (Bayer, G.P. 114841; B.P. 24296, 1899). The affinity for cotton is increased by acyl substitution, the

substituted ureas (II) obtained by the action of phesgeno being a good example (*see* Battegay and Wolff, Bull. Soc. chim. 1923, [iv], 33, 1481).



I.



II.

(For further details, *see* DYESTUFFS, Azo, Vol. IV, 215c, 216a, c).

Certain of the technically important acids are described in detail below; information concerning the remainder is summarised in the tables.

**1-Amino-2-naphthol-4-sulphonic Acid** is formed by fusion of  $\alpha$ -naphthylamine-2:4-disulphonic acid with caustic soda (Tomieka, J.S.C.I. 1917, 36, 1043). It is prepared in 82–84% yield from 1-nitroso- $\beta$ -naphthol by action of sodium bisulphite followed by concentrated sulphuric acid (Fieser, Organic Syntheses, 1931, XI, 12). It is also formed from 1-amino-2-naphthol by the action of sodium sulphite in presence of air (Marschalk, Bull. Soc. chim. 1929, [iv], 45, 651).

In technical practice the acid is diazotised immediately, and may be isolated as the diazo-oxido (*see* Battegay and Schmidt, *ibid.* 1927, [iv], 41, 205).

**Properties.**—The acid,  $\text{HA} + \frac{1}{2}\text{H}_2\text{O}$ , forms very sparingly soluble needles.

**Reactions.**—In alkaline solution the acid is readily oxidised by air (Dahl, G.P. 82097; B.P. 5153, 1895). The *diazo-oxide*, exposed to light in presence of enough acid to prevent coupling with the decomposition product, decomposes quantitatively into 1:2-dihydroxynaphthalene-4-sulphonic acid (Schmidt and Maier, Ber. 1931, 64 [B], 767). Chlorinated or brominated in sulphuric acid the *diazo-oxide* gives the 6-halogen derivative, which by action of cupreous oxide is converted into the 6-halogen-2-naphthol-4-sulphonic acid (Battegay, Silbermann, and Kienzlo, Bull. Soc. chim. 1931, [iv], 49, 716; Ruggli and Michels, Helv. Chim. Acta, 1931, 14, 779); nitrated it gives the 6-nitro-1-diazo-2-naphthol-4-sulphonic acid (Ruggli, Knapp, Merz, and Zimmermann, *ibid.* 1929, 12, 1034), an important dyestuff intermediate. The *diazo-oxide*, and other naphthaleno-1:2-diazo-oxides, when treated with sodium sulphite form coloured additive products which when heated decompose giving 2-naphthol-1-sulphonic acids. Thus 2-naphthol-1:4- and 1:6-disulphonic acids can be obtained (Krebster and Vannotti, *ibid.* 1938, 21, 1221). Chlorination of the aminonaphtholsulphonic acid itself gives a chloramino as intermediate product (Pilz and Krackiewicz, Roczn. Chem. 1931, 11, 40; *see also* Hellor et al., Z. anorg. Chem. 1930, 43, 1131).

**1-Amino-2-naphthol-6-sulphonic Acid** is not itself of importance, but its O-methyl and O-ethyl ethers find technical application as middle components in disazo-dyes for cotton (*v. Dyestuffs*, Azo, Vol. IV, 222). They are prepared by nitrating 2-methoxy(or ethoxy)-naphthalene-6-sulphonic acid and reducing the nitro-compound (Cassella, G.P. 58306; Bayer, G.P. 69155). 1-Amino-2-methoxy(or ethoxy)-naphthalene-6-sulphonic acid is sparingly soluble, the sodium salt freely soluble in water. The necessary 2-alkoxynaphthalene-6-sulphonic acids are formed by sulphonating  $\beta$ -naphthyl alkyl ethers with chlorosulphonic acid in an inert medium (Amphlett and Armstrong, Chem. News, 1887, 55, 8; Lapworth, *ibid.* 1895, 71, 205).

**1-Amino-2-alkoxynaphthalene-7-sulphonic Acids** are obtained similarly (Cassella, Bayer, *l.c.*) but are not technically important as the 2-alkoxynaphthalene-7-sulphonic acids are not readily accessible.

**1-Amino-8-naphthol-4-sulphonic Acid (S-acid)** may be obtained from 1:8-diamino-naphthalene-4-sulphonic acid by the bisulphite method in presence of acetone (Bucherer, J. pr. Chem. 1904, [ii], 70, 349). It is prepared from  $\alpha$ -naphthylamine-4:8-disulphonic acid by fusion with caustic potash at 210° (Badische, G.P. 63074; B.P. 20275, 1891; Bayer, G.P. 75317), and isolated from the dissolved melt as the free acid by acidification.

**Properties.**—The acid forms sparingly soluble needles. The alkali salts are readily soluble, showing a bluish-green fluorescence in solution. With ferric chloride an emerald-green coloration is produced. The alkaline solution is oxidised slowly in air.

**Reactions.**—The acid may be diazotised giving a sparingly soluble diazo-compound (Cassella, G.P. 82676). It may be coupled, both in acid and in alkaline solution, with diazotised bases and can be used as a middle component in disazo-dyes (Badische, G.P. 91855; B.P. 9894, 1893). With excess of bromine in acetic acid it gives 2:4:7-tribromo-1-amino-5:8-naphthoquinone, m.p. 235° (Heller *et al.*, *l.c.*—this paper describes the action of bromine on other aminonaphthol-sulphonic acids).

**1-Amino-8-naphthol-3:6-disulphonic Acid (H-acid)** has been obtained from 1:8-diaminonaphthalene-3:6-disulphonic acid by hydrolysis with 10% sulphuric acid at 100–120° or with 40% caustic soda at 200°; or from 1:8-dinitronaphthalene by heating with sodium bisulphite solution at 90–100°. It is prepared from  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid by fusion with caustic soda solution at 180–190°; addition of ammonia is recommended as preventing hydrolysis of the amino-group (Newport Co., U.S.P. 1573056). The acid is isolated as the acid sodium salt by acidification of the dissolved melt at suitable dilution.

**Properties.**—The acid is sparingly soluble in cold water. The acid sodium salt,  $\text{NaHA} + \frac{1}{2}\text{H}_2\text{O}$ , and the acid barium salt,  $\text{BaH}_2\text{A}_2 + 4\frac{1}{2}\text{H}_2\text{O}$ , form somewhat sparingly soluble needles (Dressel and Kothe, Ber. 1894, 27, 2150). Solutions give a brownish-red coloration with ferric chloride. The acid forms sparingly soluble salts with arylamines (1 mol.)

or arylenediamines ( $\frac{1}{2}$  mol.), which may be used for identification (Forster and Mosby, J.S.C.I. 1928, 47, 157r). A method of detecting the acid by means of such salts has been suggested (Lynch, Ind. Eng. Chem. 1922, 14, 964).

**Reactions.**—The acid may be diazotised forming a yellow diazo-compound. In both acid and alkaline solution it couples with diazotised bases, forming two series of monoazo-dyes. It is widely used in the dyestuffs industry for azo-dyes. On bromination in aqueous solution it gives a violet coloured *quinhydrone* (Heller *et al.*, *l.c.*).

**2-Amino-5-naphthol-7-sulphonic Acid (J-acid)** has been obtained from 1:6-dihydroxy-naphthalene-3-sulphonic acid by the bisulphite method (Badische, G.P. 117471; B.P. 1387, 1900). It is prepared from  $\beta$ -naphthylamine-5:7-disulphonic acid by fusion with 50% caustic soda solution under pressure at 190°, being isolated as the free acid by acidification of the dissolved melt.

**Properties.**—The acid is very sparingly soluble in water. The alkali salts are readily soluble, their solutions readily becoming discoloured in air by oxidation. Solutions give a brownish-black precipitate with hot ferric chloride.

**Reactions.**—The acid may be diazotised in suspension giving a yellow diazo-compound. In both acid and alkaline solution it couples with diazotised bases, forming two series of monoazo-dyes. It may be halogenated in the 1-position (Bayer, G.P. 254715; 258299; B.P. 14152, 14153, 1912). *Acetyl-J-acid* (Du Pont, U.S.P. 2062368) with chlorosulphonic acid gives the sulphonyl chloride (I.G., B.P. 326226). With phenylhydrazines and sodium hydrogen sulphite, carbazole derivatives are formed (Bucherer and Zimmermann, J. pr. Chem. 1921, [ii], 103, 277). Important derivatives are *carbonyl-J-acid*, by reaction of phosgene on J-acid, and *phenyl-J-acid* (2-anilino-5-naphthol-7-sulphonic acid) by interaction of aniline and sodium bisulphite with J-acid; both are used in the manufacture of direct cotton dyes.

**2-Amino-8-naphthol-6-sulphonic Acid ( $\gamma$ -acid)** has been obtained from 1:7-dihydroxy-naphthalene-3-sulphonic acid by heating with 30% ammonia under pressure at 120–150°, or by the bisulphite reaction. It is prepared from  $\beta$ -naphthylamine-6:8-disulphonic acid by fusion with caustic soda at 190–195° being isolated as the free acid by acidification of the dissolved melt.

**Properties.**—The acid forms very sparingly soluble needles. The alkali and alkaline earth salts are readily soluble, the solutions oxidising slowly in air and giving a dirty claret colour with ferric chloride solution.

**Reactions.**—The acid may be diazotised in suspension forming a sparingly soluble yellow diazo-compound. In both acid and alkaline solution it couples with diazotised bases forming two series of monoazo-dyes. On halogenation it is substituted in the 1-position (Bayer, *l.c.*). With phenylhydrazine and sodium hydrogen sulphite, carbazole derivatives are formed (Bucherer and Zimmermann, *l.c.*). An important derivative is *phenyl- $\gamma$ -acid* (2-anilino-8-naphthol-6-sulphonic acid), obtained by the action of aniline and sodium bisulphite on  $\gamma$ -acid.

## AMINONAPHTHOLMONOSULPHONIC ACIDS.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S 1:2:4	See text (p. 353c).	See text (p. 353d).
1:2:5	Reduction of azo derivatives of $\beta$ -naphthol-5-sulphonie acid (Witt, Ber. 1888, 21, 3478).	Acid, very sparingly soluble. Gives brown coloration with ferric chloride.
1:2:6	(1) Reduction of nitroso- $\beta$ -naphthol-6-sulphonic acid by tin and hydrochloric acid (Meldola, J.C.S. 1881, 39, 47). (2) Reduction of azo-derivatives of $\beta$ -naphthol-6-sulphonic acid (Witt, Ber. 1888, 21, 3475).	Acid, HA, sparingly soluble needles; sodium salt (Elkonogen), NaA + 2 $\frac{1}{2}$ H <sub>2</sub> O. Solutions, especially if alkaline, are very sensitive to air. Gives brown coloration with ferric chloride. For diazo-oxide, cf. Gelgy, l.c. below. Couples with diazotised bases (cf. Aktlenges., G.P. 79103; B.P. 13833, 1893). For O-alkyl ethers, see p. 354a.
1:2:7	Reduction of azo derivatives of $\beta$ -naphthol-7-sulphonic acid (Witt, <i>ibid.</i> 1888, 21, 3477).	Acid, very sparingly soluble needles. Gives brown coloration with ferric chloride. For diazo-oxide, cf. Gelgy, G.P. 171024. Couples with diazotised bases (cf. Aktlenges., l.c.).
1:2:8	Reduction of azo derivatives of $\beta$ -naphthol-8-sulphonic acid (Witt, Ber. 1888, 21, 3474).	Acid, very sparingly soluble leaflets. Gives brown coloration with ferric chloride. For diazo-oxide, cf. Gelgy, l.c.
1:3:4 (4:2:1)	1-Amino-3-naphthol sulphonated with monohydrate (Friedländer and Rudt, <i>ibid.</i> 1896, 29, 1609).	Acid, very sparingly soluble needles. Converted by water at 120° into 1:3-dihydroxy-naphthalene.
1:3:6 (4:2:7)	Mixed with 1:6:3-acid, by boiling $\alpha$ -naphthylamine-3:6-disulphonic acid with 75% caustic potash solution (Cassella, G.P. 82670).	Acid, very sparingly soluble; sodium salt separated by salting out from the 1:6:3-isomer. Forms a readily soluble diazo-compound. Couples in alkaline solution with diazotised bases (Cassella, l.c.).
1:4:2 (4:1:3)	Reduction of nitroso or azo derivatives of $\alpha$ -naphthol-3-sulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1281) (cf. 2:1:3).	No description published. N-aryl derivatives as intermediates for dyes (Sandez, B.P. 639078).
1:4:3 (4:1:2)	(1) 1-Amino-4-naphthol sulphonated with 10% anhydro-acid at 30-40° (Seidel, <i>ibid.</i> 1892, 25, 424; cf. Friedländer and Reinhardt, <i>ibid.</i> 1894, 27, 239). (2) Reduction of nitroso (Conrad and Fischer, Annalen, 1893, 273, 114) or of azo derivatives (Reverdin and de la Harpe, Ber. 1892, 25, 1403) of $\alpha$ -naphthol-2-sulphonic acid.	Acid, HA, very sparingly soluble needles which give a grass-green solution in alkalis or alkali carbonates, rapidly becoming brown. Oxidised by dilute nitric acid to [ $\alpha$ -naphthoquinone-3-sulphonic acid and phthalic acid; by permanganate in alkaline solution to phthalic acid (Seidel, l.c.).
1:4:5 (4:1:8)	(1) Reduction of azo derivatives of $\alpha$ -naphthol-8-sulphonic acid (Reverdin and de la Harpe, <i>ibid.</i> , p. 1404). (2) Electrolytic reduction of $\alpha$ -nitronaphthalene-5-sulphonic acid in sulphuric acid solution (Gatterman, <i>ibid.</i> 1893, 26, 1852; Bayer, G.P. 81021).	Acid, leaflets soluble in water but insoluble in cold alcohol, solution in ammonia yellow; lead and barium salts sparingly soluble in water (Bayer, l.c.).
1:4:6 (4:1:7)	Electrolytic reduction of $\alpha$ -nitronaphthalene-6-sulphonic acid in sulphuric acid solution (Bayer, l.c.).	Acid, needles soluble in water or cold alcohol, solution in ammonia yellow; lead and barium salts soluble in water (Bayer, l.c.).
1:4:7 (4:1:6)	Electrolytic reduction of $\alpha$ -nitronaphthalene-7-sulphonic acid in sulphuric acid solution (Bayer, l.c.).	Acid, needles soluble in water or cold alcohol solution in ammonia yellow; lead and barium salts soluble in water (Bayer, l.c.).
1:5:2 (5:1:6)	(1) $\alpha$ -Naphthylamine - 2:5 - disulphonic acid digested with 50% caustic soda solution at 240-270° (Landshoff, B.P. 6195, 1890; G.P.a. 4479). (2) From 1:5-diaminonaphthalene-2-sulphonic acid by bisulphite reaction (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii], 80, 213).	Acid, sparingly soluble needles. Gives green coloration with ferric chloride (cf. Bayer, G.P. 75317). Forms a sparingly soluble diazo-compound. Couples with diazotised bases (cf. Cassella, G.P. 82670).
1:5:4 (5:1:8)	(1) From 1-acetyl amino-5-aminonaphthalene-4-sulphonic acid; or from (2) 1:5-Dihydroxynaphthalene - 4 - sulphonic acid by the bisulphite reaction (Bucherer <i>ibid.</i> , p. 223).	Acid, HA, crystallises in needles. Couples with diazotised bases forming azo-dyes.
1:5:6 (5:1:2)	1-Amino-5-naphthol sulphonated with sulphuric acid below 100° (Aktlenges., G.P. 68504).	Acid, very sparingly soluble needles. Gives blue coloration with ferric chloride. Forms greenish-yellow solution with nitrous acid. Couples with diazotised bases.

AMINONAPHTHOLMONOSULPHONIC ACIDS—*continued*.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S 1:5:7 (5:1:3) M-acid.	(1) $\alpha$ -Naphthylamine-5:7-disulphonic acid heated with 75% caustic soda solution at 170° (Badische, G.P. 73276; B.P. 2370, 1893). (2) 1:5-Diaminonaphthalene-3-sulphonic acid heated with water under pressure at 160° (Cassella, G.P. 85058). (3) From 1:5-dihydroxynaphthalene-7-sulphonic acid by the bisulphite reaction (Badische, G.P. 117471; B.P. 1387, 1900). (4) 1-Amino-5-naphthol-2:7-disulphonic acid heated with 10% sulphuric acid under pressure at 135° (Cassella, G.P. 188505).	<i>Acid</i> and <i>sodium</i> salt, sparingly soluble leaflets. Gives black coloration with ferric chloride. Forms a deep orange-yellow sparingly soluble <i>diazo</i> -compound (cf. Cassella, G.P. 82676). Couples in alkaline solution with diazotised bases (cf. Badische G.P. 75327; 82572; B.P. 2370, 1893). With phenylhydrazine and sodium hydrogen sulphite <i>carbazole</i> derivatives are formed (Bucherer and Zimmermann, J. pr. Chem. 1921, [ii], 103, 277).
1:5:8 (5:1:4)	From 1:5-diaminonaphthalene-4-sulphonic acid by the bisulphite reaction (Bucherer and Uhlmann, l.c., p. 226).	<i>Acid</i> , HA+3½H <sub>2</sub> O. Couples with diazotised bases forming azo-dyes.
1:6:3 (6:2:7)	(1) Mixed with 1:3:6-acid, by boiling $\alpha$ -naphthylamine-3:6-disulphonic acid with 75% caustic potash solution (Cassella, G.P. 82676). (2) 1-Amino-6-naphthol-3:5-disulphonic acid boiled with dilute acids (Cassella, G.P.a. 5163).	<i>Acid</i> , sparingly soluble, <i>sodium</i> salt readily soluble. Forms a yellow sparingly soluble <i>diazo</i> -compound. Couples with diazotised bases (cf. Cassella, G.P. 82676).
1:6:4 (5:2:8)	$\alpha$ -Naphthylamine-4:6-disulphonic acid fused with caustic soda at 180–200° (Dahl, G.P. 68232; Friedländer and Kielbasinski, Ber. 1896, 29, 1979).	<i>Acid</i> , sparingly soluble needles; <i>sodium</i> salt, NaA, needles; <i>barium</i> salt, prisms, readily soluble. Gives brownish coloration with ferric chloride. Forms a sparingly soluble <i>diazo</i> -compound. Couples with diazotised bases (cf. Cassella, G.P. 82676).
1:6:8 (5:2:4)	Nitration of O-acyl derivatives of 2-naphthol-4-sulphonic acid, hydrolysis and reduction.	<i>Sodium</i> salt, sparingly soluble (Gelgy, B.P. 553535).
1:7:3 (8:2:6)	Mixed with a more soluble isomer, by heating $\alpha$ -naphthylamine-3:7-disulphonic acid with 40% caustic soda under pressure at 200° (Cassella, G.P. 57007; 58352).	<i>Acid</i> , very sparingly soluble needles; <i>sodium</i> salt readily soluble leaflets. Forms a very sparingly soluble <i>diazo</i> -compound. Couples with diazotised bases, giving two series of monoazo-dyes (Cassella, l.c.).
1:7:4 (8:2:5)	1-Amino-7-naphthol sulphonated with sulphuric acid below 30° (Cassella, G.P. 75066).	<i>Acid</i> , sparingly soluble; alkali salts readily soluble. Forms a sparingly soluble <i>diazo</i> -compound. Couples in alkaline solution with diazotised bases (cf. Cassella, l.c. Bayer, G.P. 198138).
1:7:5 (8:2:4)	Acyl derivatives of $\beta$ -naphthol-4-sulphonic acid are nitrated and reduced. After removing the 1:6:8-isomer as sparingly soluble sodium salt, the solution is acidified to precipitate the 1:7:5-acid (Gelgy, B.P. 553535).	
1:8:2 (8:1:7)	(1) $\alpha$ -Naphthylamine-2:8-disulphonic acid fused with caustic soda at 170–220° (Cassella, G.P. 75710). (2) 1-Amino-8-naphthol-2:4-disulphonic acid boiled with 50% sulphuric acid (Cassella, G.P. 75710).	<i>Acid</i> , sparingly soluble radiate prisms. Forms a dark brown sparingly soluble <i>diazo</i> -compound. Couples with diazotised bases (cf. Cassella, G.P. 82676).
1:8:3 (8:1:6)	(1) $\alpha$ -Naphthylamine-3:8-disulphonic acid fused with caustic alkali below 210° (Bayer, G.P.a. 4723; B.P. 13443, 1890). (2) 1-Amino-8-naphthol-3:5-disulphonic acid boiled with dilute sulphuric acid at 140° (Leonhardt, G.P.a. 8626; B.P. 19253, 1895; Cassella, G.P. 108848).	<i>Acid</i> , sparingly soluble prisms or needles; <i>sodium</i> salt readily soluble. Forms an orange-yellow sparingly soluble <i>diazo</i> -compound. Couples with diazotised bases (cf. Cassella, G.P. 82676).
1:8:4 (8:1:5) S-acid.	See text (p. 354a).	See text (p. 354b).
1:8:5 (8:1:4)	(1) From 1:8-diaminonaphthalene-5-sulphonic acid either by boiling with 20% sulphuric acid (Cassella, G.P. 73607; B.P. 4613, 1893), or by the bisulphite method (Bayer, G.P. 109102; B.P. 16807, 1899). (2) $\alpha$ -Naphthylamine-5:8-disulphonic acid heated with 75% caustic potash solution at 150° (Bayer, G.P. 75055; B.P. 15269, 1893).	<i>Acid</i> , very sparingly soluble needles; <i>sodium</i> and <i>potassium</i> salts readily soluble, showing violet fluorescence in solution (Cassella, l.c.). The <i>calcium</i> salt is easily soluble (Badische, G.P. 77937). Gives dirty green coloration with ferric chloride (Bayer, G.P. 75055). Forms a readily soluble yellow <i>diazo</i> -compound (Cassella, l.c.).

## AMINONAPHTHOLMONOSULPHONIC ACIDS—continued.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S 1:8:5 (8:1:4)	(3) 8 - Chloro- $\alpha$ -naphthylamine - 5 - sulphonic acid heated with 50% caustic soda solution under pressure at 190° (Badische, G.P. 112778). (4) Mixed with 1:8:7 acid, when 1-amino-8-naphthol is sulphonated with sulphuric acid at 15–20° (Badische, G.P. 62289; B.P. 9676, 1890; G.P. 77937; 84951).	Couples in acid or in alkaline solution with diazotised bases, being used as a middle component for diazo-dyes (cf. Badische, G.P. 81241; 114900). For benzoyl derivative and azo-dyes therefrom, cf. Badische, G.P. 54662; B.P. 9676, 1890).
1:8:6 (8:1:3)	(1) 1:8-Diaminonaphthalene-3-sulphonic acid heated with 15% sulphuric acid at 120° (Cassella, G.P. 70780; B.P. 6972, 1891; cf. Cassella, G.P. 73607). (2) $\alpha$ - Naphthylamine - 6:8 - disulphonic acid heated with 50% caustic potash solution under pressure at 200° (Bayer, G.P. 80853; B.P. 15269, 1893). (3) 1-Amino-8-naphthol-4:6-disulphonic acid boiled with zinc dust and dilute caustic soda solution (Kalle, G.P. 233934).	Acid, sparingly soluble needles; sodium and potassium salts readily soluble; barium salt, needles (Bayer, l.c.). Gives green coloration with ferric chloride (Bayer, l.c.). Forms a yellow sparingly soluble diazo-compound (Bayer, l.c.). Couples in alkaline solution with diazotised bases (cf. Bayer, G.P. 82074; 85389; B.P. 15269, 1893).
1:8:7	1-Amino-8-naphthol sulphonated with 75% sulphuric acid at 130–160° (Badische, G.P. 82900) or (mixed with 1:8:5-acid) with sulphuric acid at 15–20° (Badische, G.P. 84951).	Acid, sparingly soluble; calcium salt almost insoluble. Forms a readily soluble diazo-compound. Couples with diazotised bases.
2:1:3	Reduction of azo-derivatives of $\alpha$ -naphthol-3-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 54).	Acid, HA, broad needles.
2:1:4*	(1) Reduction of azo (König, <i>ibid.</i> 1890, 23, 808) or nitroso derivatives of $\alpha$ -naphthol-4-sulphonic acid (Witt and Kaufmann, <i>ibid.</i> 1891, 24, 3162). (2) Action of sodium bisulphite on 2-nitroso- $\alpha$ -naphthol (Schmidt, J. pr. Chem. 1891, [II], 44, 531; cf. Bönlger, Ber. 1894, 27, 29) or [ $\beta$ ]-naphthoquinone- $\beta$ -chlorimide (Friedländer and Reinhardt, <i>ibid.</i> 1891, 27, 242).	Acid, HA, sparingly soluble needles (Friedländer and Reinhardt, l.c.). Forms a violet-black dyestuff by oxidation with air (Reverdin and de la Harpe, G.P. 63043; B.P. 16377, 1891). Not diazotisable in acid solution (cf. Cassella, G.P. 82676), but in absence of acid, gives diazo-oxide (cf. Gelgy, G.P. 171024; B.P. 10235, 1904).
2:1:5*	Reduction of azo derivatives of $\alpha$ -naphthol-5-sulphonic acid (Gattermann and Schulze, <i>ibid.</i> 1897, 30, 51; cf. Reverdin and de la Harpe, <i>ibid.</i> 1893, 26, 1280).	Acid, HA, sparingly soluble scales or needles. Diazotisable in absence of free mineral acid giving diazo-oxide (cf. Gelgy, G.P. 171024; B.P. 10235, 1904).
2:1:7	Reduction of 2-nitro- $\alpha$ -naphthol-7-sulphonic acid (Finger, J. pr. Chem. 1909, [II], 79, 444).	Acid, HA + 2H <sub>2</sub> O, needles; alkaline solution becomes dark green on exposure to the air.
2:1:8	Reduction of 2-nitroso- $\alpha$ -naphthol-8-sulphonic acid with iron and ferrous chloride (I.C.I., B.P. 417861).	Acid, sparingly soluble colourless needles; alkaline solution on oxidation gives a characteristic deep green colour.
2:3:6 (3:2:7)	(1) $\beta$ - Naphthylamine - 3:6 - disulphonic acid heated with 75% caustic soda at 230–250° (Höchst, G.P. 53076; B.P. 15176, 1899; Friedländer and Zakrzewski, Ber. 1894, 27, 763). (2) 2:3 - Dihydroxynaphthalene - 6 - sulphonic acid heated with ammonia at 150–160° (Aktienges., G.P. 62964; cf. Oesterle, J.S.C.I. 1898, 17, 836).	Acid, very sparingly soluble needles; sodium salt leaflets; barium salt, BaA <sub>2</sub> , sparingly soluble. Gives dark blue coloration with ferric chloride (Höchst, l.c.). Forms an orange diazo-compound (cf. Höchst, l.c.; Cassella, G.P. 109932; B.P. 28107, 1897). Couples in alkaline solution with diazotised bases (cf. Aktienges., G.P. 84145).
2:4:6 (3:1:7)	$\alpha$ -Naphthol-3:7-disulphonic acid heated with ammonia under pressure at 180° (Kalle, G.P. 94079).	Acid, sparingly soluble leaflets; alkali salts readily soluble. Forms a yellow diazo-compound. Couples with diazotised bases.
2:4:7 (3:1:6)	(1) $\beta$ - Naphthylamine - 4:7 - disulphonic acid heated with 35% caustic alkali at 200° (Bayer, G.P. 7978; B.P. 25214, 1894). (2) $\alpha$ -Naphthol-3:6-disulphonic acid heated with ammonia under pressure at 180° (Kalle, G.P. 94079).	Acid, moderately soluble leaflets; alkali salts readily soluble. Forms a yellow diazo-compound. Couples in alkaline solution with diazotised bases (cf. Bayer, l.c.).
2:4:8	$\beta$ -Naphthylamine-4:8-disulphonic acid fused with 80% caustic alkali at 215° (Bayer, G.P. 8070; B.P. 3580, 1895).	Acid, sparingly soluble needles; alkali salts easily soluble. Gives no coloration with ferric chloride. Forms a yellow sparingly soluble diazo-compound. Couples in alkaline solution with diazotised bases.

\* An acid containing the sulphonie group in either the 4- or 5-position is produced when 2-amino-1-naphthol is sulphonated with 10% anhydro-acid at 40°. It is sparingly soluble and gives a brown coloration with ferric chloride (Reverdin and de la Harpe, Ber. 1893, 26, 1280; Kern and Sandoz, G.P. 69228).

## AMINONAPHTHOLMONOSULPHONIC ACIDS—continued.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S 2:5:(6) 6:1:(2)) and 2:5:(8) (6:1:(4))	2-Amino-5-naphthol sulphonated with sulphuric acid at 20–30° (Bayer, G.P.a. 7372; B.P. 5267, 1894) forms two acids about which little is known, the yield of the less soluble being 30%.	One of the acids gives a dirty precipitate, the other, a bluish-grey precipitate with ferric chloride. Each acid forms a yellow <i>diazo</i> -compound and couples with diazotised bases.
2:5:1 (6:1:5)	$\beta$ -Naphthylamine-1:5-disulphonic acid fused with caustic alkali at 210–230° (Kalle, G.P. 233105; 242052; B.P. 9743; 9744, 1910).	<i>Acid</i> , moderately soluble needles. Gives brownish-red <i>diazo</i> -compound. Couples in alkaline solution. In acid solution loses its sulphonic group in coupling. On sulphonation gives 2:5-aminonaphthol-1:6- and -6:8-disulphonic acids. Boiled with dilute mineral acids it gives 2:5-aminonaphthol. Gives 1:6- <i>dihydroxynaphthalene</i> -5-sulphonic acid by the bisulphite method and in the presence of ammonia 1:6-diaminonaphthalene-5-sulphonic acid (Bucherer and Wahl, J. pr. Chem. 1921, [ii], 103, 129).
2:5:7 (6:1:3) J-acid.	See text (p. 354c).	See text (p. 354c).
2:5:8	1:6-Dihydroxynaphthalene-4-sulphonic acid heated with 28% ammonia under pressure at 140–180° (Dahl, G.P. 70285; B.P. 4110, 1892).	<i>Acid</i> , sparingly soluble; <i>alkali</i> salts readily soluble. Gives brown coloration with ferric chloride. Forms a yellow sparingly soluble <i>diazo</i> -compound. Couples in acid or in alkaline solution with diazotised bases (Dahl, l.c.; G.P. 67258).
2:6:4	Reduction of 6-nitro-2-naphthol-8-sulphonic acid (Jacchia, Annalen, 1902, 323, 124).	<i>Acid</i> , HA + H <sub>2</sub> O, sparingly soluble needles. Forms a yellow sparingly soluble <i>diazo</i> -compound.
2:6:8 (6:2:4)	Reduction of 6-nitro-2-naphthol-4-sulphonic acid (Ruggli and Zimmermann, Helv. Chim. Acta, 1930, 13, 256).	Couples with diazotised bases to form dyes.
2:7:(3) (7:2:(6))	2:7 - Dihydroxynaphthalenesulphonic acid heated with 30% ammonia under pressure at 120–150° (Aktienges., G.P. 63956).	<i>Acid</i> , very sparingly soluble; <i>alkali</i> salts easily soluble. Gives greenish-black coloration with ferric chloride. Forms a yellow sparingly soluble <i>diazo</i> -compound. Couples in acid or in alkaline solution with diazotised bases.
2:7:? (7:2:?)	Partial hydrolysis of the disulphonic acid formed from 2-amino-7-naphthol by sulphonation with sulphuric acid at 30° (Cassella, G.P. 131526).	<i>Acid</i> , needles; <i>sodium</i> salt, NaA + H <sub>2</sub> O, sparingly soluble. Gives violet precipitate with ferric chloride. Forms a yellow sparingly soluble <i>diazo</i> -compound. Couples in acid or in alkaline solution with diazotised bases, giving two series of mono-azo-dyes.
2:8:(5) (7:1:(4)) 2:8:(7) (7:1:(2))	2-Amino-8-naphthol sulphonated with sulphuric acid at 30° forms two acids in about equal proportion (Bayer, G.P.a. 7335; B.P. 5148, 1894).	"Sch." acid, readily, "Y" acid, sparingly soluble; separated by adding acid to solution of mixed calcium salts. Each acid forms a yellow soluble <i>diazo</i> -compound and couples with diazotised bases.
2:8:6 (7:1:3) Y-acid.	See text (p. 354d).	See text (p. 354d).

## AMINONAPHTHOLDISULPHONIC ACIDS.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S:S 1:2:3:6	Reduction of azo derivatives of $\beta$ -naphthol-3:6-disulphonic acid (Witt, G.P. 49857; Ber. 1888, 21, 3479).	<i>Acid sodium</i> salt, NaHA, readily soluble needles. Gives dark brown coloration with ferric chloride. Diazotisable in absence of mineral acid giving <i>diazo-oxide</i> (cf. Geigy, G.P. 171024). Does not couple with diazotised bases.

## AMINONAPHTHOLDISULPHONIC ACIDS—continued.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S:S 1:2:3:7	Reduction of 1-nitroso- $\beta$ -naphthol-3:7-disulphonic acid (Gelgy, G.P. 171024; B.P. 10235, 1904).	Acid, sparingly soluble; alkaline solutions greenish-yellow. Diazotisable in absence of mineral acid giving diazo-oxide (cf. Gelgy, l.c.).
1:2:4:6	Interaction of 1-nitroso- $\beta$ -naphthol-6-sulphonic acid and sulphurous acid (Bönlger, Ber. 1894, 27, 3052).	Acid sodium salt, NaHA, readily soluble needles. Diazotisable in absence of mineral acid giving diazo-oxide (cf. Gelgy, l.c.).
1:2:4:7	Sulphonation of 1-amino-2-naphthol-4-sulphonic acid with monohydrate below 100° (Grelschelm, G.P.a. 15414; 15820; B.P. 3655, 1908).	Acid sodium salt, NaHA, very soluble, shows in solution bluish-green fluorescence like the acid sodium salt of the 4:6-disulphonic acid, with which it may be identical.
1:2:4:7	Interaction of 1-nitroso- $\beta$ -naphthol-7-sulphonic acid and sulphurous acid (Bönlger, Ber. 1894, 27, 3052).	Acid sodium salt, NaHA, sparingly soluble needles. Diazotisable in absence of mineral acid giving diazo-oxide (cf. Gelgy, l.c.).
1:2:6:8	Reduction of azo derivatives of $\beta$ -naphthol-6:8-disulphonic acid (Witt, G.P. 49857; Ber. 1888, 21, 3981).	Acid sodium salt, NaHA, easily soluble prisms. Gives dark brown coloration with ferric chloride. Forms diazo-oxide (cf. Gelgy, l.c.).
1:4:3:6 (4:1:2:7)	(1) Reduction of azo derivatives of $\alpha$ -naphthol-2:7-disulphonic acid (Reverdin and de la Harpe, <i>ibid.</i> 1892, 25, 1405). (2) Electrolytic reduction of $\alpha$ -nitronaphthalene-3:6-disulphonic acid (Bayer, G.P. 81621).	Acid, sparingly soluble needles; sodium salt readily soluble. Gives a dark red coloration with ferric chloride (Bayer, l.c.). Is not diazotisable (cf. Reverdin and de la Harpe, Ber. 1893, 26, 1281).
1:4:3:7 (4:1:2:6)	Electrolytic reduction of $\alpha$ -nitronaphthalene-3:7-disulphonic acid (Bayer, G.P. 81621).	Barium salt, sparingly soluble. Gives a rose-red coloration with ferric chloride.
1:4:3:8 (4:1:2:5)	Reduction of 4-nitroso- $\alpha$ -naphthol-2:5-disulphonic acid (Friedländer, Ber. 1895, 28, 1530).	Acid, readily soluble needles. Is not diazotisable, and does not couple with diazotised bases.
1:5:2:7 (5:1:3:6)	$\alpha$ -Naphthylamino-2:5:7-trisulphonic acid heated with 50% caustic potash at 180–200° (Bayer, G.P.a. 7901; B.P. 17141b, 1893; Cassella, G.P. 188505).	Acid sodium salt, moderately soluble needles. Gives wine-red coloration with ferric chloride. Forms an orange-red soluble diazo-compound, which with sodium carbonate solution becomes sky-blue and then orange.
1:5:3:7 (5:1:3:7)	Fusion of $\alpha$ -naphthylamine-3:5:7-trisulphonic acid with caustic soda at 160–170° (Cassella, G.P. 75432).	Acid and acid sodium salt readily soluble (Cassella, G.P. 84952). Gives dark-green coloration with ferric chloride (Cassella, G.P. 81952). Forms an orange diazo-compound. Couples in alkaline solution with diazotised bases (cf. Cassella, l.c.; G.P. 83011).
1:5:(4):(6) 5:1:(2):(8)	1-Amino-5-naphthol sulphonated with 23% anhydro-acid at 100° (Aktenges., G.P.a. 3767).	Acid and sodium salt readily soluble. Forms a yellow diazo-compound. Couples with diazotised bases.
1:6:3:5 (5:2:1:7)	1-Amino-6-naphthol-3-sulphonic acid sulphonated with 12% anhydro-acid below 20° (Cassella, G.P.a. 5163; cf. G.P. 84952).	Acid sodium salt readily, calcium salt sparingly soluble. Gives violet-black coloration with ferric chloride. Forms a yellow soluble diazo-compound. Couples in acid or alkaline solution with diazotised bases, but gives only one series of monoazo-dyes.
1:6:3:7 (5:2:3:7)	1-Amino-6-naphthol-3-sulphonic acid heated with sulphuric acid at 140–150° or the 3:5-disulphonic acid heated with sulphuric acid at 150° (Cassella, G.P. 84952).	Acid sodium salt, sparingly soluble needles. Gives greenish-black coloration with ferric chloride. Forms a soluble diazo-compound. Couples in alkaline solution with diazotised bases (cf. Cassella, l.c.; G.P. 95988).
1:7:(4):? (8:2:(5):?)	1-Amino-7-naphthol sulphonated with sulphuric acid above 100° (Cassella, G.P. 69458; cf. G.P. 75066).	Acid readily soluble.
1:8:2:4 (8:1:5:7) 2 S-acid. Chicago Acid.	Fusion of naphthasultam-2:4-disulphonic acid (" $\alpha$ -naphthylamine-2:4:8-trisulphonic acid") with 90% caustic soda at 170° (Aktenges., G.P.a. 3340; B.P. 2984, 1893; Bayer, G.P. 79566; 80668; B.P. 4979, 1893; Cassella, G.P. 75710; Dressel and Kothe, Ber. 1894, 27, 2141).	Acid readily soluble; acid sodium salt, NaHA + H <sub>2</sub> O, easily soluble needles; calcium salt moderately soluble. Gives a greenish-black coloration with ferric chloride. Forms a reddish-yellow soluble diazo-compound. Couples in acetic acid or in alkaline solution with diazotised bases giving only one series of monoazo-dyes, but in HCl solution, disazo-dyes of the 4-monosulphonic acid may be formed (cf. Bayer, G.P. 77703; B.P. 4979, 1893).



Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S:5 1:8:(2):(5) 8:1:(4):(7)	1:8 - Diaminonaphthalene - (2):5 - disulphonic acid boiled with 20% sulphuric acid (Cassella, G.P. 73048).	<i>Acid</i> moderately, <i>acid sodium</i> salt readily soluble. Gives brown coloration with ferric chloride. Forms yellow <i>diazo</i> -compound. Couples with diazotised bases (cf. Cassella, G.P. 84952).
1:8:2:2? (8:1:7:7)	1:8 - Diaminonaphthalenetrisulphonic acid boiled with water or 10% sulphuric acid (Fischesser, G.P.a. 7595; B.P. 13203, 1894).	<i>Acid sodium</i> salt, NaHA, moderately soluble. Gives green coloration with ferric chloride. Forms a soluble yellow <i>diazo</i> -compound. Couples in acid solution with diazotised bases.
1:8:3:5 (8:1:4:6)	1-Amino-8-naphthol-3-sulphonic acid sulphonated with monohydrate at the ordinary temperature (Leonhardt, G.P.a. 8626; B.P. 19253, 1895; Cassella, G.P. 108848).	<i>Acid</i> and <i>acid sodium</i> salt sparingly soluble. Forms a yellow sparingly soluble <i>diazo</i> -compound. Couples in acid or alkaline solution with diazotised bases, forming two series of monoazo-dyes (cf. Cassella, l.c.).
1:8:3:6 (8:1:3:6) H-acid.	See text (p. 354b).	See text (p. 354b).
1:8:4:6 (8:1:3:5) K-acid.	Fusion of $\alpha$ -naphthylamine-4:6:8-trisulphonic acid with 70% caustic soda under pressure at 175° (Bayer, G.P. 80741; B.P. 171410, 1893; Kalle, G.P. 99164; B.P. 515, 1894).	<i>Acid sodium</i> salt readily soluble needles, (Bayer, l.c.). Gives yellowish-green coloration with ferric chloride. Forms a readily soluble yellow <i>diazo</i> -compound. Couples in acid or alkaline solution with diazotised bases forming two series of monoazo-dyes (cf. Kalle, l.c.; G.P. 108266).*
1:8:4:(7) (8:1:(2):5)	1-Amino-8-naphthol-4-sulphonic acid sulphonated with 23% anhydro-acid at the ordinary temperature (Aktienges., G.P.a. 3918; Badische, G.P. 125696; B.P. 18366, 1900).	<i>Acid sodium</i> salt sparingly soluble needles. Gives brownish-black coloration with ferric chloride. Forms a yellowish-brown <i>diazo</i> -compound. Couples with diazotised bases (cf. Aktienges., l.c.).
1:8:5:7 (8:1:2:4)	1-Amino-8-naphthol-5-sulphonic or 7-sulphonic acid sulphonated with monohydrate at 100° (Badische, G.P. 62289; B.P. 9676, 1890; cf. Badische, G.P. 82900).	<i>Acid</i> readily soluble leaflets; <i>acid sodium</i> salt readily soluble. Gives blue coloration with ferric chloride. Forms a sparingly soluble yellow <i>diazo</i> -compound. Couples with diazotised bases (cf. Cassella, G.P. 84952).
1:8:(5):2? (8:1:(4):7)	Fusion of naphthasultamdisulphonic acid D with 90% caustic soda at 170° (Bayer, G.P. 80668; B.P. 4979, 1893).	<i>Acid sodium</i> salt moderately soluble needles. Gives green coloration with ferric chloride. Couples with diazotised bases.
2:1:3:6	Reduction of 2-nitroso- $\alpha$ -naphthol-3:6-disulphonic acid (Geigy, G.P. 171024; B.P. 10235, 1904).	<i>Acid sodium</i> salt easily soluble needles. Diazotisable in absence of mineral acid giving a <i>diazo-oxide</i> (cf. Geigy, l.c.).
2:1:3:8	Reduction of azo derivatives of $\alpha$ -naphthol-3:8-disulphonic acid (Berntsen, Ber. 1890, 23, 3093).	Diazotisable in absence of mineral acid giving a <i>diazo-oxide</i> (cf. Geigy, l.c.). As component in dyes, Gesellsch., B.P. 249884.
2:1:4:6	Reduction of azo derivatives of $\alpha$ -naphthol-4:6-disulphonic acid (Reverdin and de la Harpe, <i>ibid.</i> 1893, 26, 1282; cf. Böniger, <i>ibid.</i> 1894, 27, 3052).	<i>Acid</i> readily soluble; <i>acid sodium</i> salt sparingly soluble needles.
2:1:4:7	Reduction of azo or nitroso derivatives of $\alpha$ -naphthol-4:7-disulphonic acid (Reverdin and de la Harpe, l.c.; cf. Böniger, l.c. 3054).	<i>Acid</i> , moderately soluble needles; <i>sodium</i> salt readily soluble. Diazotisable in absence of mineral acid giving a <i>diazo-oxide</i> (cf. Geigy, l.c.).
2:1:4:8	Reduction of azo derivatives of $\alpha$ -naphthol-4:8-disulphonic acid (Reverdin and de la Harpe, l.c., 1283).	<i>Acid</i> and <i>acid sodium</i> salt moderately soluble. Diazotisable in absence of mineral acid giving a <i>diazo-oxide</i> (cf. Geigy, l.c.). As component in dyes, Gesellsch., B.P. 249884.
2:3:6:8 (3:2:5:7)	Sulphonation of 2-amino-3-naphthol-6-sulphonic acid (Aktienges., G.P. 86448; B.P. 8645, 1895).	No description published.

\* The coloration produced by the interaction of K-acid with sulphanilic acid in the presence of nitrous acid forms a delicate test for minute quantities of nitrites in water (Erdmann, Ber. 1900, 33, 213).

## AMINONAPHTHOLDISULPHONIC ACIDS—continued.

Constitution.	Preparation.	Acids, salts, and reactions.
N:O:S:5 2:4:6:8 (3:1:5:7)	Digestion of $\beta$ -naphthylamine-4:6:8-trisulphonic acid with 60% caustic soda at 170–180° (Bayer, G.P.a. 8154; G.P. 80242).	<i>Acid sodium salt</i> , moderately soluble. Gives bluish-green coloration with ferric chloride. Forms a pale yellow <i>diazo</i> -compound. Couples with diazotised bases.
2:5:1:7 (6:1:3:5)	Digestion of $\beta$ -naphthylamine-1:5:7-trisulphonic acid with 60% caustic soda at 160–220° (Bayer, G.P. 80878; B.P. 20580, 1893).	<i>Acid sodium salt</i> readily soluble needles. Gives green coloration with ferric chloride. Forms an orange-yellow soluble <i>diazo</i> -compound. Couples in alkaline solution with diazotised bases (cf. Bayer, G.P. 92708; B.P. 1062, 1894).
2:5:3:7 (6:1:3:7)	$\beta$ -Naphthylamine - 3:5:7 - trisulphonic acid heated with 30% caustic soda at 190° (Oehler, G.P. 158147; B.P. 1581, 1904).	<i>Acid sodium salt</i> easily soluble. Gives yellowish-brown coloration with ferric chloride. Forms an easily soluble orange <i>diazo</i> -compound. Couples in alkaline solution with diazotised bases.
2:6:5:8 (6:2:1:4)	From 6-nitro-1-diazo-2-naphthol-4-sulphonic acid heated with sodium sulphite and copper sulphate followed by reduction of the nitro-group (Krebs and Vannotti, Helv. Chim. Acta, 1938, 21, 1231).	<i>Monosodium salt</i> , +H <sub>2</sub> O, microcrystalline powder. <i>Alkali salts</i> show a strong green fluorescence in aqueous solution. Gives a violet coloration with ferric chloride quickly changing to green.
2:7:3:6 (7:2:3:6)	(1) $\beta$ -Naphthylamine-3:6:7-trisulphonic acid heated with 55% caustic soda at 180–240° (Bayer, G.P.a. 7019; B.P. 17141, 1893; cf. Bayer, G.P. 80878). (2) 2:7 - Dihydroxynaphthalene - 3:6 - disulphonic acid heated with 23% ammonia at 180–220° (Aktenges., G.P. 75142, B.P. 16190, 1893). (3) 2-Amino-7-naphthol sulphonated with sulphuric acid at 30° (Cassella, B.P. 131526).	<i>Acid</i> sparingly soluble; <i>acid sodium salt</i> sparingly soluble needles. Gives deep violet coloration with ferric chloride (Bayer, l.c.; Aktenges., l.c.). Forms a sparingly soluble yellow <i>diazo</i> -compound (Cassella, l.c.). Couples only slowly or not at all with diazotised bases (Cassella, l.c.).
2:8:3:6 (7:1:3:6)	Fusion of $\beta$ -naphthylamine-3:6:8-trisulphonic acid with 80% caustic soda at 220–260° (Höchst, G.P. 53023; B.P. 15175, 1889).	<i>Acid and salts</i> readily soluble. Gives dark green coloration with ferric chloride. Forms a yellow sparingly soluble <i>diazo</i> -compound. Couples in alkaline solution with diazotised bases (cf. Aktenges., G.P. 108215; B.P. 14895, 1893). With chlorosulphonic acid gives a <i>disulphonyl chloride</i> , yellow crystals, darkening above 250° (I.G., B.P. 331590).

## AMINONAPHTHOLTRISULPHONIC ACIDS.

1-Amino-2-naphthol and 2-Amino-1-naphthol-3:6:8-trisulphonic Acids are obtained by reduction of azo derivatives of the corresponding  $\beta$ -naphthol- and  $\alpha$ -naphthol-3:6:8-trisulphonic acids. They give *diazo-oxides* on diazotisation in absence of mineral acid (Geigy, G.P. 171024; B.P. 10235, 1904).

1-Amino-8-naphthol-2:4:6-trisulphonic Acid, obtained by fusing naphthasultam-2:4:6-trisulphonic acid with 85% caustic potash at 150–160°, forms a sparingly soluble *acid potassium salt*, gives a green coloration with ferric chloride, also a readily soluble orange *diazo*-compound, and couples with diazotised bases (Bayer, G.P. 84597).

## NITROAMINONAPHTHOLSULPHONIC ACIDS.

The *nitroamino- $\alpha$ -naphthol*, obtained from 2:4-dinitro- $\alpha$ -naphthol by reduction with ammonium sulphide, forms yellow needles, m.p. 130° (Ebell, Ber. 1875, 8, 564).

(i) (?) - Nitro - 1 - amino - 2 - naphthol - 4 -

sulphonic Acid.—If nitrosulphuric acid, containing sufficient anhydride to remove water formed in the reaction, is added to a suspension of 1-amino-2-naphthol-4-sulphonic acid in monohydrate at 0° nitration, instead of oxidation, occurs. The nitro-compound formed, yellowish-brown needles, yields a *diamino-2-naphthol-4-sulphonic acid* on reduction and, when diazotised, a *diazo-oxide* closely resembling the 6-nitro-1-diazo-2-naphthol-4-sulphonic acid of G.P. 164655 in properties (Kalle, G.P. 249724).

(ii) 3-Nitro-1-amino-4-naphthol-6-sulphonic Acid, obtained from 2:4-dinitro-1-naphthol-7-sulphonic acid (Naphthol Yellow S) by reduction with stannous chloride and hydrochloric acid (Finger, J. pr. Chem. 1909, [ii], 79, 442) forms sparingly soluble golden yellow scales. It is diazotisable (Gesellschaft, G.P. 189513; B.P. 7535, 1906). When boiled with copper powder in alcohol it gives *copper 2-nitro-1-naphthol-7-sulphonate* (Finger, l.c.).

(iii) 4-Nitro-2-amino-1-naphthol-7-sulphonic Acid is obtained when Naphthol Yellow S in ammoniacal solution is reduced

with sodium sulphide at 90–95°. It forms yellow crystals, sparingly soluble in cold water and can be diazotised (Gesellsch., B.P. 487718).

(iv) (8)-Nitro-2-amino-3-naphthol-6-sulphonic Acid has been prepared by adding sodium nitrate to a solution of 2-amino-3-naphthol-6-sulphonic acid in sulphuric acid at 5°. It forms yellow needles. Its *sodium* and *potassium* salts are easily soluble, and it can be diazotised (Cassella, G.P. 110369; 111933).

#### NITRODIAZONAPHTHOLSULPHONIC ACIDS.

Although in some cases nitro-1-amino-2-naphthol- or nitro-2-amino-1-naphtholsulphonic acids have not been described, the corresponding diazo-compounds can be obtained by nitrating *o*-diazo-naphtholsulphonic acids. 6-Nitro-1-diazo-2-naphthol-4-sulphonic acid (Geigy, G.P. 164655; B.P. 15418, 1904) forms pale yellow crystals and couples with phenols and amines forming azo-dyes (Geigy, G.P. 169683; B.P. 15982, 1904; cf. also p. 353d). Nitro-2-diazo-1-naphtholsulphonic acids are obtained from the diazo derivative of the aminonaphtholsulphonic acids by nitration with mixed acid (Gesellsch., B.P. 491398). Nitro-1-diazo-2-naphthol-6-sulphonic and nitro-2-diazo-1-naphthol-5-sulphonic acids give azo-dyes in which, with alkaline reducing agents, the nitro-radical can be converted into a diazotisable amino-group (Kalle, G.P. 176619). Coupled with *a*-naphthol and reduced, the resultant colours are after-chrome wool dyestuffs (Gesellsch., U.S.P. 1521206).

#### DIAMINONAPHTHOLS.

These have no technical application. The free bases have only been isolated in three cases, being very rapidly oxidised on exposure of their solutions to air. A tabular summary is given of the hydrochlorides, the acetyl derivatives by which they may be characterised, and their sulphonic acids.

NH<sub>2</sub>:NH<sub>2</sub>:OH

1:3:4  
(2:4:1)

Not isolated. Obtained by reduction of 2:4-dinitro-*a*-naphthol with tin and hydrochloric acid. *Hydrochloride*, B<sub>2</sub>HCl, scales, and *sulphate*, B<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, needles, are both rapidly oxidised in air to diimino-*a*-naphthol (Graebe and Ludwig, Annalen, 1870, 154, 312); *triacetyl* derivative, needles, m.p. 280° decomp. (Meersem, Ber. 1888, 21, 1196).

The 7-sulphonic acid, obtained by reduction of Naphthol Yellow S, gives a hydrochloride, B<sub>2</sub>HCl, in needles (Gaess, *ibid.* 1899, 32, 232; cf. Lauterbach, *ibid.* 1881, 14, 2028), is not diazotisable, does not couple (cf. Aktienges., G.P. 86448; B.P. 8645, 1895), and is readily oxidised to the diimino-compound (Lauterbach, l.c.; Gaess, l.c.).

Unknown. The 7-sulphonic acid, obtained by digesting 1:3-diamino-naphthalene - 5:7-disulphonic acid with 60% caustic soda solution at 210°, couples with diazotised base Kalle, G.P. 92239).

Unknown. The 6-sulphonic acid, obtained similarly from 1:3-diamino-naphthalene - 6:8-disulphonic acid, couples with diazotised bases (Kalle, G.P. 92239).

Not isolated. Obtained by reduction of diacetyl-4-nitro-1-amino-2-naphthol, or of azo derivatives of 1-amino-2-naphthol; is rapidly oxidised to blue oxazine in the air (Nietzki and Becker, Ber. 1907, 40, 3397; cf. Kalle, G.P. 195901). *Hydrochloride*, B<sub>2</sub>HCl, needles; *N*-diacetyl derivative, m.p. 250–260°, decomp. (Kehrmann and Hertz, *ibid.* 1896, 29, 1417).

The 6-sulphonic acid, obtained by reduction of azo derivative of 1-amino-2-naphthol-6-sulphonic acid, forms a *hydrochloride*, B<sub>2</sub>HCl (Nietzki and Becker, l.c.; Kalle, l.c.).

The 8-sulphonic acid, obtained by reduction of Crocein Yellow, forms a *hydrochloride*, B<sub>2</sub>HCl, needles, readily oxidised to the diimino derivative, and is diazotisable (Nietzki and Zübelen, *ibid.* 1889, 22, 455).

Not described. Obtained by reduction of acetyl-4-nitro-1-amino-8-naphthol (Fichter and Gageur, *ibid.* 1906, 39, 3336). The 6-sulphonic acid is obtained by reduction of the azo-dye aniline → 1-amino-5-naphthol-7-sulphonic acid (Gesellsch., B.P. 399097).

Unknown. The 7-sulphonic acid, obtained by fusing 1:5-diaminonaphthalene-3:7-disulphonic acid with 90% caustic soda solution at 200–240°, forms needles sparingly soluble in hot water, and couples with diazotised bases (Cassella, G.P. 91000).

Not isolated. Obtained by reduction of 8-nitro-4-nitroso-*a*-naphthol (Friedländer and Scherzer, cf. J.S.C.I. 1900, 19, 339; Graebe and Oeser, Annalen, 1904, 335, 155); or of azo derivatives of 1-amino-8-naphthol (Fichter and Gageur, Ber. 1906, 39, 3333). *Hydrochloride*, B<sub>2</sub>HCl; *N*-diacetyl derivative, needles, m.p. 247°; *triacetyl* derivative, m.p. 258° (Fichter and Gageur, l.c.).

M.p. 194° (cf. Cassella, G.P. 117298; B.P. 16149, 1899). Obtained by reduction of 1:6-dinitro-*β*-naphthol (Loewe, Ber. 1890, 23, 2543; Kehrmann and Matis, *ibid.* 1898, 31, 2413). *Hydrochloride*, B<sub>2</sub>HCl, needles; *N*-diacetyl derivative, needles, m.p. 235°; *triacetyl* derivative, needles, m.p. 203° (Loewe, l.c.; see also Ruggli and Zimmermann, Helv. Chim. Acta, 1930, 13, 748).

NH<sub>2</sub>:NH<sub>2</sub>:OH

1:2:3  
(3:4:2)

Unknown. The 6-sulphonic acid is obtained by reduction of azo-dyes from 2-amino-3-naphthol-6-sulphonic acid (Cassella, G.P. 233939; B.P. 15646, 1910).

1:2:4

Unknown. *Diacetyl methyl ether*, m.p. 254° (Henriques, Ber. 1892, 25, 3067); *ethenyl* derivative, needles, m.p. 179° (Heermann, J. pr. Chem. 1892, [ii], 45, 552).

1:2:5

5:6:1)

Unknown. 7-Sulphonic acid obtained by reduction of azo-dye formed by coupling diazotised *p*-nitroaniline with 2-amino-5-naphthol-7-sulphonic acid in acid solution (Bayer, G.P. 172319; B.P. 1675, 1905).

1:2:7

(7:8:2)

Not described. Obtained by reduction of 7-hydroxy-*β*-l-naphthaquinonedioxime. *Hydrochloride*, B<sub>2</sub>HCl; *triacetyl* derivative, m.p. 244–245° (Nietzki and Knapp, Ber. 1897, 30, 1124).

1:2:8

(7:8:1)

Not isolated. Obtained by reduction of sulphonanilazo-2-amino-8-naphthol (Badische, G.P. 90212; B.P. 15953, 1896).

The 4-, 5-, 6-mono-, and 3:6- and 5:7-di-sulphonic acids have been obtained from the corresponding 2-amino-8-naphtholsulphonic acids (cf. Badische, l.c.), and the 6-monosulphonic acid from 2-amino-8-naphthol-6-sulphonic acid (Bayer, G.P. 87900; B.P. 6035, 1893) by reducing the azo-dyes formed by coupling with diazotised bases.

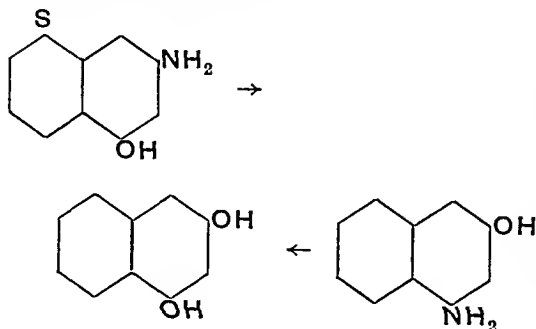
1:6:2

NH<sub>2</sub>:NH<sub>2</sub>:OH

- Presumably the 4-sulphonic acid of this diamine is obtained by reduction of nitro-1-amino-2-naphthol-4-sulphonic acid (Kalle, G.P. 249724) Scales, m.p. 220° (decomp.). Obtained by reduction of the azo derivative of 7-amino-2-naphthol (Cassella, G.P. 117298; B.P. 16140, 1899). Sulphate, sparingly soluble (Cassella, G.P. 117298; B.P. 16149, 1899); N-diacetyl derivative, needles, m.p. 226°; triacetyl derivative, needles (Kehrmann and Wolff, Ber. 1000, 33, 1540).
- 1:7:2 Not isolated. Obtained by reduction of 1-amino-7-nitroso-8-naphthol. Hydrochloride, B<sub>2</sub>HCl, needles; triacetyl derivative, needles, m.p. 234° (Fichter and Gagenr, *ibid.* 1906, 39, 3338).
- 1:7:8 (2:8:1) The 3:6-disulphonic acid, obtained by reduction of an azo derivative of 1-amino-8-naphthol-3:6-disulphonic acid, is not diazotisable in acid solution (Höchst, G.P. 02012). The 4-mono- and 4:6-di-sulphonic acids, obtained similarly from azo derivatives of 1-amino-8-naphthol-4-mono- and 4:6-di-sulphonic acids, are, like the 3:6-disulphonic acid, photographic developers (Schultz, G.P. 101953).
- 1:8:4 (4:5:1) Not isolated. Obtained by reduction of 5-nitro-4-nitroso- $\alpha$ -naphthol (Friedländer and Seherzer, *cf.* J.S.C.I., 1900, 19, 339; Graebe and Oeser, *Annalen*, 1904, 335, 152). Hydrochloride, B<sub>2</sub>HCl.
- 2:3:8 (6:7:1) Unknown. The 6-sulphonic acid, obtained by digesting 2:3-diamino-naphthalene-6:8-disulphonic acid with 00% caustic potash solution at 190–200° forms an azimino derivative with nitrous acid, and couples with diazotised bases (Aktenges., G.P. 86448; B.P. 8645, 1895).
- 2:6:1 Not isolated. Obtained by reduction of 6-nitronaphthalene-2-diazo-1-oxide. Triacetyl derivative, needles, m.p. 261°, decomp. (Gaess and Ammelburg, Ber. 1804, 27, 2213).
- 2:7:8 (2:7:1) Unknown. The 6-sulphonic acid, obtained by reduction of an azo derivative of 2-amino-8-naphthol-6-sulphonic acid, is not diazotisable in acid solution (Höchst, G.P. 02012).

## DIHYDROXYNAPHTHALENES.

With the exception of the 1:2, 1:3, and 1:4 derivatives the dihydroxynaphthalenes may be obtained from the corresponding naphthalene-disulphonic acids or naphtholmonosulphonic acids by fusion with caustic alkali. Another, less general, method consists in heating diaminonaphthalenes, aminonaphthols, or aminonaphtholsulphonic acids with dilute mineral acids under pressure, whereby the amino-radical is replaced by hydroxyl and the sulphonic group, when present, eliminated:



The bisulphite method may also be used with diaminonaphthalenes and aminonaphthols for the same purpose.

1:2- and 1:4-dihydroxynaphthalenes are prepared by reduction of the respective naphthaquinones.

All the possible ten dihydroxynaphthalenes are known. They are easily soluble in caustic alkali solution, but only sparingly in cold water. Alkaline solutions rapidly oxidise in air, becoming dark in colour.

Heated with ammonia under pressure the four  $\alpha\beta$ -dihydroxynaphthalenes give  $\beta$ -amino- $\alpha$ -naphthols as intermediate products.

In the reaction of 1:2-, 1:4-, 1:5-, and 2:7-dihydroxynaphthalene with bisulphite, leading to formation of an additive intermediate, one, at least, of the hydroxyl groups probably undergoes tautomeric change to the ketonic form. The reaction, in presence of ammonia, may be used to prepare aminonaphthols (Fuchs and Stix, Ber. 1922, 55, [B], 658; Fuchs and Pirak, *ibid.* 1926, 59, [B], 2454).

With nitrous acid the heteronuclear dihydroxynaphthalenes yield mononitroso-compounds, which, when the nitroso-group occupies the *ortho*-position, furnish lakes with chromium or iron salts. The nitroso derivative formed from the monoalkyl ether of 1:8-dihydroxynaphthalene is said closely to resemble 2-nitroso- $\alpha$ -naphthol, and that from the 2:6- or 2:7-dihydroxy derivative, 1-nitroso- $\beta$ -naphthol in properties.

Many of the dihydroxynaphthalenes form molecular compounds with amines (Kremann, Hommelmayr, and Riemer, *Monatsh.* 1922, 43, 164; Briner and Kuhn, *Helv. Chim. Acta*, 1929, 12, 1075). The 1:2- and 2:3-dihydroxynaphthalenes increase the electrical conductivity of boric acid, the latter having the greater effect (Böeseken, Anema, and Brevet, *Rec. trav. Chim.* 1922, 41, 778).

Of the dihydroxynaphthalenes, the most important for dyestuffs technology is the 1:5-isomer, which enters into the composition of important mordant dyes giving fast black chromed shades on wool; sulphonic acids of the 1:8-isomer are also used for making such azo-dyes.

(i) 1:2-Dihydroxynaphthalene is obtained by reducing  $[\beta]$ -naphthaquinone with sulphurous acid in the cold. It is also obtained by heating 1-amino-2-naphthol-6:8-disulphonic acid with water under pressure above 200° (Bayer, G.P. 89242).

*Identification.*—It forms scales, m.p. 60°, dissolves in alkalis forming yellow solutions, which turn green in air, and, in aqueous solution, have a severe caustic action on the skin. The diacetate forms scales, m.p. 110°; the 1-methyl ether, monoclinic plates, m.p. 90.5°; the dimethyl ether, m.p. 31°, b.p. 278–280° (Bezdzik and Friedländer, *Monatsh.* 1909, 30, 280).

*Reactions.*—It couples with diazotised bases forming azo-dyes, which give red to bluish-violet lakes with aluminium or chromium salts. In aqueous solution it is oxidised by ferric chloride, giving  $[\beta]$ -naphthaquinone (Zincke, *Annalen*, 1892, 268, 275). With nitric acid ( $\rho$  1.48) it yields 3-nitro- $[\beta]$ -naphthaquinone.

(ii) 1:3-Dihydroxynaphthalene is obtained by boiling 1-amino-3-naphthol with dilute acid (Friedländer, Ber. 1895, 28, 1952); or by heating 1-amino-3-naphthol-4-sulphonic acid with water or dilute acid at 120° (Friedländer and Rüdtt, *ibid.* 1896, 29, 1609); or by heating 2-amino-4-naphthol-8-sulphonic acid, 1:3-dihydroxynaphthalene-7-mono-, or -5:7-disulphonic acid with 5% sulphuric acid at 235°.

**Identification.**—It crystallises from water in scales, m.p. 124°. It is almost insoluble in benzene. In alkaline solution it is rapidly oxidised. With ferric chloride it gives a yellow-brown precipitate. The *diacetate*, prisms, has m.p. 56°.

**Reactions.**—It couples with diazotised bases in alkaline or weakly acid solution, giving azo-dyes characterised by their yellow colour. By digestion with 60% caustic soda solution at 180–200° it is converted into *o-toluic acid* (Kalle, G.P. 79028). When heated with aqueous ammonia at 130–140° it yields 2-amino-4-naphthol or 1:3-diaminonaphthalene, and with aniline, 2-anilino-4-naphthol. Condensed with phthalic anhydride and either phosphoric oxide at 130° or zinc chloride at 200°, it gives *naphthylfluorescein* (Bayer, G.P. 84990; B.P. 3497, 1895).

(iii) 1:4-Dihydroxynaphthalene is prepared by reducing [α]-naphthaquinone with sulphurous acid, or with tin and boiling aqueous hydrochloric acid.

**Identification.**—It crystallises in needles, m.p. 176°, and is readily soluble in alcohol, ether or boiling water; sparingly so in benzene. On oxidation it yields [α]-naphthaquinone. The *diacetate* forms tablets, m.p. 128–130°. The *monomethyl ether*, needles, m.p. 131°, is obtained by the action of 18% methyl-alcoholic hydrogen chloride in the cold; the *monoethyl ether*, needles, m.p. 105° is prepared by boiling with 3% ethyl-alcoholic hydrogen chloride (Badische, G.P. 173730; B.P. 7287A, 1906; Russig, J. pr. Chem. 1900, [ii], 62, 50). These ethers may also be obtained by heating 1-amino-4-naphthol hydrochloride with the alcohol under pressure at 170–180° (Höchst, G.P. 234411). The monoethers couple with diazotised aminosulphonic acids to form *ortho*-azo-dyes (Badische, G.P. 176640; B.P. 7287, 1906). The *dimethyl ether* forms needles, m.p. 85°.

With ammonium sulphite and ammonia 1:4-dihydroxynaphthalene gives 1:4-aminonaphthol (Fuchs and Pirak, Ber. 1926, 59 [B], 2454).

(iv) 1:5-Dihydroxynaphthalene is formed by melting potassium α-naphthol-5-sulphonate with caustic potash at 200–250°, but is usually manufactured by heating sodium naphthalene-1:5-disulphonate with caustic soda at 220–260°. It may be obtained by heating 1:5-diaminonaphthalene or 1-amino-5-naphthol with 4% hydrochloric acid under pressure at 180°; or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii], 69, 84). It is an important dyestuffs intermediate.

**Identification.**—It crystallises from water in scales, m.p. 265°, sublimes in needles, is almost insoluble in benzene, reduces silver solution, and, in alkaline solution, becomes dark brown on exposure to air. The *diacetate*, m.p. 159–160°, forms feathery crystals; the *dibenzoate*, m.p.

235°, scales (Fischer, *ibid.* 1916, [ii], 94, 14); the *monomethyl ether*, m.p. 140°, leaflets; the *dimethyl ether*, m.p. 183–184°, needles.

**Reactions.**—It couples with most diazotised bases forming *para*-azo-dyes but the *ortho*-azo-compound with diazotised *o*-aminophenols (Fischer and Bauer, *ibid.* 1917, [ii], 95, 265; v. Vol. IV, p. 1986). With nitrous acid it gives the 2-nitroso derivative (Read, Holliday & Co., G.P. 68809; B.P. 1812, 1890). Oxidised with chromic acid it gives *juglone* (5-hydroxy-[α]-naphthaquinone). Sulphonated with sulphuric acid at 50–60° it yields a mixture of the 2- and 4-monosulphonic acids; at 100–160° it gives a *disulphonic acid*. Digested with ammonia at 250–300°, or by the bisulphite reaction, it yields 1:5-diaminonaphthalene. The *diacetate* chlorinated in carbon tetrachloride at room temperature gives the 4:8-dichloro derivative, m.p. 143°, from which 4:8-dichloro-1:5-dihydroxynaphthalene, m.p. 194°, is obtained by hydrolysis (Wheeler and Mattox, J. Amer. Chem. Soc. 1933, 55, 686). Bromination of the dihydroxynaphthalene in acetic acid gives the 2:6-dibromo derivative (*diacetate*, m.p. 228°); bromination of the *diacetate* gives 2:4:6:8-tetrabromo-1:5-diacetoxynaphthalene (Wheeler and Ergle, *ibid.* 1930, 52, 4872). Heated with potassium hydrogen carbonate under pressure at 230°, a *dicarboxylic acid*, m.p. 300°, probably the 2:6 derivative, is formed (Hemmelmayer, Monatsh. 1922, 43, 61).

(v) 1:6-Dihydroxynaphthalene may be obtained by desulphonation of 1:6-dihydroxynaphthalene-4-sulphonic acid with sodium amalgam. It is prepared by fusion of sodium naphthalene-1:6-disulphonate with caustic soda at 230–250° (Ewer and Pick, G.P. 45229); or from β-naphthol-5-sulphonic acid by fusion with caustic potash and a little water at 260°.

**Identification.**—It crystallises from benzene in small prisms or serrated scales, m.p. 137–138°, sublimes in scales, is only sparingly soluble in water and with ferric chloride gives a transient blue coloration. The *diacetate*, m.p. 73°, forms prisms; the *dimethyl ether*, m.p. 60–61°, needles; the *diethyl ether*, m.p. 83°, needles (Fischer and Bauer, J. pr. Chem. 1916, [ii], 94, 2).

**Reactions.**—It couples with diazobenzene in acid solution to give a mono-, in pyridine solution a bis-, and in strongly alkaline solution a tris-azo-compound (Fischer and Bauer, *l.c.*). With nitrous acid it gives mainly the red 2-nitroso derivative, with some of the yellow 4-nitroso-compound. Digested with ammonia at 150–300° it gives 1:6-diaminonaphthalene. Heated with mixed potassium carbonate-bicarbonate, in absence of water it gives a *monocarboxylic acid* (Hemmelmayer, Monatsh. 1917, 38, 86). Heated with an equal weight of phthalic anhydride at 180–200° it gives 3:11-dihydroxynaphthylfluoran, which forms oxonium salts with acids (Fischer and König, Ber. 1917, 50, 1011; Höchst, G.P. 275897; König, Chem.-Ztg. 1914, 38, 483), but, if boric acid is present, the product is 1:6-dihydroxynaphthoyl-*o*-benzoic acid, which has a particularly sweet taste (Gesellsch., G.P. 311213).

(vi) 1:7-Dihydroxynaphthalene may be obtained by fusing  $\beta$ -naphthol-8-sulphonic acid with caustic potash (Bayer, G.P. 53915; B.P. 14230, 1889); or, in 70–80% yield, by heating 1:7-dihydroxynaphthalene-3-mono-, or -3:6-disulphonic acid, or 2-amino-8-naphthol-6-mono-, or -3:6-di-sulphonic acid with dilute sulphuric acid under pressure at 185–200° (I.G., B.P. 366600).

**Identification.**—It crystallises in needles, m.p. 178°, is moderately soluble in water and readily soluble in benzene. Its alkaline solution rapidly oxidises in air, turning black. With ferric chloride it gives, at first, a white turbidity which with more reagent becomes blue (Friedländer and Zinberg, Ber. 1896, 29, 40). The *diacetate*, m.p. 108°, forms rhombic tables.

**Reactions.**—In alkaline solution it couples with diazotised *o*-aminophenolsulphonic acids giving monoazo-dyes. With nitrous acid it gives a *mononitroso* derivative (Bayer, G.P. 53915). The sodium salt heated with carbon dioxide under pressure at 140° gives 1:7-dihydroxy- $\beta$ -naphthoic acid (Heyden, G.P. 55414).

(vii) 1:8-Dihydroxynaphthalene is obtained by fusing naphthasultone or  $\alpha$ -naphthol-8-sulphonic acid with 75% caustic potash at 220–230° (Erdmann, Annalen, 1888, 247, 356); or by heating  $\alpha$ -naphthylamine-8-sulphonic acid with 9% caustic soda solution under pressure at 220–260°; or from 1:8-diaminonaphthalene by hydrolysis with 17% hydrochloric acid under pressure at 180°. It is conveniently prepared by heating 1:8-dihydroxynaphthalene-4-sulphonic acid with 20% sulphuric acid at 160–200° (Heller and Kretzschmann, Ber. 1921, 54 [B], 1098; cf. Bayer, B.P. 13665, 1889).

**Identification.**—It crystallises in long needles, m.p. 140°, or with  $1\text{H}_2\text{O}$  in scales, oxidises rapidly, when moist, in air, is only sparingly soluble in water, but readily soluble in benzene. With ferric chloride it gives a white flocculent precipitate which rapidly turns green. The *diacetate*, m.p. 147–148°, forms scales.

**Reactions.**—In acid solution it couples with diazotised bases to form 4-mono-azo-dyes (Badische, G.P. 51559); in alkaline or dilute acetic acid solution it gives 4:7-disazo-dyes (Friedländer and Silverstern, Monatsch., 1902, 23, 518). With nitrous acid it yields a *mononitroso* derivative. It cannot readily be nitrated, but its diacetyl derivative yields 2:4-dinitro-8-acetoxy- $\alpha$ -naphthol (Calvet and Carnero, J.C.S. 1936, 556). On oxidation with chromic acid it yields 5-hydroxy-[ $\alpha$ ]-naphthaquinone; with peracetic acid, a resinous product, but the methyl ether with the latter yields 8-methoxy-[ $\alpha$ ]-naphthaquinone, together with, possibly, 7-methoxyindenone-2-carboxylic acid (Böeseken and Smitt, Rec. trav. chim. 1939, 58, 125). The sodium salt, heated with carbon dioxide under pressure at 140°, yields 1:8-dihydroxy- $\beta$ -naphthoic acid (Heyden, G.P. 55414). Warmed with sulphuric acid at 50° it gives a mixture of three disulphonic acids (Badische, G.P. 79029; 79030; B.P. 14294, 1891).

Condensed with acyl chlorides or anhydrides in presence of zinc chloride at 140–150°, yellow or orange dihydroxyketones (e.g., 1:8-dihydroxy-

2-acetonaphthone, needles, m.p. 100–101°, and benzonaphthone, needles, m.p. 121–122°) are obtained. These form lakes with alumina (Lange, G.P. 126199; 129035; 129036).

(viii) 2:3-Dihydroxynaphthalene is obtained by fusing  $\beta$ -naphthol-3:6-disulphonic acid or 2:3-dihydroxynaphthalene-6-sulphonic acid with 90% caustic soda at 280–320° (Badische, G.P. 57525); or by hydrolysing the latter with 25% sulphuric acid at 200°; also by heating 2-amino-3-naphthol-6-sulphonic acid with dilute mineral acid under pressure at 180–200° (Höchst, B.P. 73076; Friedländer and Zakrzewski, Ber. 1894, 27, 762).

**Identification.**—It forms monoclinic scales (Siegmund, Monatsch. 1908, 29, 1087), m.p. 160–161°, sparingly soluble in water, giving with ferric chloride a dark blue coloration or precipitate. The *monomethyl ether*, m.p. 108°, forms needles; the *dimethyl ether*, m.p. 115–116°, needles; the *monoethyl ether*, m.p. 109–110°; the *diethyl ether*, m.p. 96–97° (Friedländer and Silberstern, Monatsch. 1902, 23, 519).

**Reactions.**—In weak acid (acetic acid) solution it couples with diazotised bases to form 1-monoazo-dyes, in alkaline solution 1:4-disazo-dyes. By the bisulphite method at 80°, or when digested with 30% ammonia at 140–150°, it gives 2-amino-3-naphthol, but at 250°, 2:3-diaminonaphthalene. It forms co-ordinated compounds with iron, aluminium, and arsenic acid. The aluminates are colourless, but, with ferric iron, two series are formed, one red (co-ordination number=6), the other violet (co-ordination number=4) (Weinland and Seuffert, Arch. Pharm. 1928, 266, 455).

(ix) 2:6-Dihydroxynaphthalene is obtained by fusing sodium naphthalene-2:6-disulphonate or sodium  $\beta$ -naphthol-6-sulphonate with caustic potash (Eimmet, Annalen, 1887, 241, 369).

**Identification.**—It forms rhomb-like scales, m.p. 218° (Willstätter and Parnas, Ber. 1907, 40, 1410), is sparingly soluble in water (1.08 g. in 1 litre at 14°) or in light petroleum. Alkaline solutions show a strong blue fluorescence. With ferric chloride a yellowish-white precipitate is formed. It has a strong caustic effect on the skin. The *diacetate*, m.p. 175°, forms scales; the *monomethyl ether*, m.p. 136°, lustrous flakes (Windaus, *ibid.* 1924, 57 [B], 1738); the *dimethyl ether*, m.p. 150°, rhomb-like scales; the *diethyl ether*, m.p. 162°, scales.

**Reactions.**—In weak acid (acetic acid) solution it couples with diazotised bases to form 1-monoazo-dyes (Kehrmann, *ibid.* 1907, 40, 1962), in alkaline solution a mixture of 1-monoazo- with disazo-dyes (Kaufler and Brauer, *ibid.* 1907, 40, 3274). With nitrous acid it gives the 1-nitroso derivative. The dimethyl ether on nitration gives the 1-nitro and 1:5-dinitro derivatives (Chakravarti and Pasupati, J.C.S. 1937, 1859). It is oxidised by lead dioxide in boiling benzene to 2:6-naphthaquinone. With ammonia at 150–300° it gives 2:6-diaminonaphthalene; with aniline at 170° 2:6-dianilinonaphthalene. It also forms additive compounds with ammonia (Briner and Kuhn, Helv. Chim. Acta, 1929, 12, 1067). With sulphuric acid at 5° it gives a



*sulphonic acid*, possibly the 4 derivative (Bayer, G.P. 72222) or the 1:5-*disulphonic acid* (Jacchia, Annalen, 1902, 323, 114); at 100° it gives a *disulphonic acid*.

(x) 2:7-Dihydroxynaphthalene is obtained by fusing sodium naphthalene-2:7-disulphonate with caustic soda at 290–300° (Weber, Ber. 1881, 14, 2206); or, similarly, from  $\beta$ -naphthol-7-sulphonic acid (Pfitzinger and Duisberg, *ibid.* 1889, 22, 398). It may also be obtained from 2:7-dihydroxynaphthalene-3:6-disulphonic acid by heating with 20% sulphuric acid at 200°.

*Identification*.—It forms needles, m.p. 190°, dissolves readily in hot water, is sparingly soluble in benzene, gives no coloration with ferric chloride, but blackens rapidly in alkaline solution. The *diacetate*, m.p. 136°, forms scales; the *dibenzoate*, m.p. 138–139°, scales; the *monomethyl ether*, m.p. 117°, needles, its *acetate*, m.p. 130°, needles, and its *nitroso-compound*, m.p. 129°, scales (Fischer and Hammerschmidt, J. pr. Chem. 1916, [ii], 94, 24); the *dimethyl ether*, m.p. 138°, tablets; the *diethyl ether*, m.p. 104°, scales.

*Reaction*.—In alkaline solution it couples with 1 mol. of diazotised bases to give 1-monoazo-dyes (Kaufler and Brauer, Ber. 1907, 40, 3274), or with 2 mol. to give 1:8-disazo-dyes (Cassella, G.P. 108166; B.P. 9502, 1899). With nitrous acid it yields the 1-*nitroso* derivative which, with iron salts, gives a *Naphthol Green* (Leonhardt, G.P. 58611). With sulphuric acid at 100° it gives 2:7-dihydroxynaphthalene-3:6-disulphonic acid. Digested with ammonia at 150–300° or by the bisulphite reaction, it yields 2:7-diaminonaphthalene. With aniline at 190° it gives 7-*anilino*-2-naphthol; with arylamines in the presence of arylamine hydrochlorides at 140–150°, 2:7-diarylamino-naphthalenes. Bromine in acetic acid gives, at 5°, the 3-*bromo*- and, at 100°, the 3:6-*dibromo*- derivative (Joffe and Fedorova, J. Gen. Chem. Russ. 1936, 6, 1079; A. 1937, II, 15).

#### DIHYDROXYNAPHTHALENESULPHONIC ACIDS.

Dihydroxynaphthalenesulphonic acids are usually obtained from naphthol-di- or -tri-sulphonic acids, from naphthylamine-di- or -tri-sulphonic acids, or from aminonaphtholsulphonic acids. The process involves fusion with 60–75% caustic soda at temperatures of the order 180–230°. The general rules found to govern these processes may be summarised as follows:

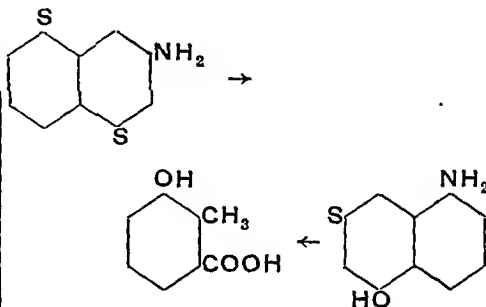
1. Replacement of amino- by hydroxyl: In  $\alpha$ -naphthylaminesulphonic acids the replacement most readily occurs when the sulphonic group is in the 3-, 4-, or 5-position. With  $\beta$ -naphthylaminesulphonic acids the exchange does not occur.

2. Replacement of sulphonic by hydroxyl:

- (a) From  $\alpha$ -naphtholsulphonic acids, the sulphonic group in the 8-position is most easily replaced, then that in position 5; that in the 2- or 4-position resists replacement. From  $\beta$ -naphtholsulphonic acids the sulphonic group in the 4-, 5-, and 8-position is easily displaced; that in 1- or 6-position resists replacement.

- (b) From  $\alpha$ -naphthylaminesulphonic acids the order of replaceability is similar to that from  $\alpha$ -naphtholsulphonic acids, the 4-sulphonic group resisting replacement as is shown by the production of 1:6-dihydroxynaphthalene-4-sulphonic acid from  $\alpha$ -naphthylamine-4:6-disulphonic acid. In the  $\beta$ -naphthylaminesulphonic acids the 4- or 5-sulphonic group is more easily replaced than that in the 8-position, otherwise the order is similar to that given by the  $\beta$ -naphtholsulphonic acids.

An important exception to these rules is the fact that fusions which might be expected to give 1:3-dihydroxynaphthalene sulphonic acids usually lead to decomposition and the formation of hydroxytoluic acids:



(Kalle, G.P. 91201; B.P. 16559, 1894; Höchst, G.P. 81281; 81333).

The  $\alpha$ -aminonaphtholsulphonic acids are converted to the dihydroxynaphthalenesulphonic acids by the action of water or dilute mineral acid (5%) under pressure at elevated temperature. With  $\beta$ -aminonaphtholsulphonic acids (except 2-amino-3-naphthol-6-sulphonic acid) the exchange takes place only when one of the other substituents, usually the hydroxyl group, is present in the 4-position. Thus 2:4-dihydroxynaphthalene-7-sulphonic acid may be prepared by fusing  $\beta$ -naphthylamine-4:7-disulphonic acid with caustic potash at 215°, followed by heating the 2:4-aminonaphthol-7-sulphonic acid thus produced with water at 200°.

Less general methods of preparation, applied in a few cases only, are the bisulphite method and reduction of [ $\alpha$ -] or [ $\beta$ -]naphthaquinonesulphonic acids.

The dihydroxynaphthalenesulphonic acids and their alkali salts are easily soluble in water, the solution made alkaline usually showing fluorescence. Heated with dilute mineral acids above 200°, many of them furnish the corresponding dihydroxynaphthalene by loss of the sulphonic acid group. They give colour reactions with ferric chloride and bleaching powder solutions by which they may be characterised. They also give characteristic azo-dyes when coupled with certain diazotised bases.

Certain of these acids, in particular the 1:8-dihydroxynaphthalene-4-sulphonic and the 2:4- and 3:6-disulphonic acids, are or have been used for the manufacture of chromable azo-dyes for wool (*v.* DYE STUFFS, Azo, Vol. IV, 204*d*).



## DIHYDROXYNAPHTHALENEMONOSULPHONIC ACIDS.

Constitution.	Preparation.	Acids, salts, and reactions.
O:O:S 1:2:4	(1) Reduction of [ $\beta$ ]-naphthaquinone-4-sulphonic acid with sulphurous acid (Witt and Kaufmann, Ber. 1891, 24, 3163). (2) Action of sodium bisulphite solution on [ $\beta$ ]-naphthaquinone (Bayer, G.P. 70867; B.P. 825, 1893). (3) Quantitatively on exposure of suspension of 1-diazo-2-naphthol-4-sulphonic acid to light (Schmidt and Maler, Ber. 1931, 64 [B], 767).	Sodium salt, needles; potassium salt, sparingly soluble prisms. Alkaline solution exposed to air turns red, forming 2-hydroxy-[ $\alpha$ ]-naphthaquinone. Nitrous acid regenerates [ $\beta$ ]-naphthaquinone-4-sulphonic acid. Does not couple (cf. Bayer, G.P. 85241).
1:2:6	Reduction of [ $\beta$ ]-naphthaquinone-6-sulphonic acid with sulphurous acid (Witt, <i>ibid.</i> 1891, 24, 3154; G.P. 50506; Paul, Z. angew. Chem. 1897, 10, 51).	Ammonium salt, $\text{NH}_4\text{A}$ , readily soluble leaflets. Couples with diazotised bases forming azo-dyes, which give lakes with chromium and other oxides (Witt, <i>l.c.</i> ; G.P. 49872).
1:2:5 1:2:7 1:2:8	These acids are obtained by reduction of the corresponding [ $\beta$ ]-naphthaquinonesulphonie acids (Witt, <i>l.c.</i> , 3157).	No description published.
1:3:5	2-Amino-4-naphthol-8-sulphonic acid heated with water at 180–200° (Bayer, G.P. 85241; B.P. 3580, 1895).	Alkali salts form yellow solutions which show green fluorescence. Gives dirty green coloration with ferric chloride. Couples with diazotised bases.
1:3:6	(1) 1-Amino-3-naphthol-6-sulphonic acid heated with water at 120° (Friedländer and Rüdert, Ber. 1896, 29, 1613). (2) 2-Amino-4-naphthol-7-sulphonic acid heated with water at 200° (Bayer, G.P.a. 7978; B.P. 25214, 1894).	Alkali salts very soluble; show green fluorescence in alkaline solution; barium salt, $\text{BaA}$ , readily soluble needles (Friedländer and Rüdert, <i>l.c.</i> ). Couples with diazotised bases (cf. Bayer, G.P. 84091; B.P. 3580, 1895).
1:3:7	1:3-Dihydroxynaphthalene-5:7-disulphonic acid heated with 5% sulphuric acid under pressure at 210° (Bayer, G.P. 90378).	Alkali salts give yellow solutions which show intense green fluorescence. Gives bluish-black coloration with ferric chloride. Couples with diazotised bases (cf. Bayer, G.P. 80100; B.P. 4962, 1895).
1:5:2	(1) Together with the 4-acid when 1:5-dihydroxynaphthalene is warmed with sulphuric acid at 50–60° (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii], 80, 235). (2) $\alpha$ -Naphthol-2:5-disulphonic acid heated with 60% caustic soda at 250° (Bayer, G.P. 68344; B.P. 3397, 1890).	Acid sodium salt, readily soluble leaflets; the alkaline solutions show blue fluorescence. Gives bluish-green coloration with ferric chloride. Couples with diazotised bases (cf. Bayer, <i>l.c.</i> ).
1:5:3	Naphthalene-1:3:5-trisulphonic acid fused with caustic alkali (Bayer, G.P. 166768; B.P. 18569, 1902).	Couples with diazotised bases (Bayer, <i>l.c.</i> ).
1:5:4	Together with the 2-acid ( <i>sec supra</i> ) when 1:5-dihydroxynaphthalene is warmed with sulphuric acid at 50–60°.	Calcium salt forms a sparingly soluble double salt with calcium sulphate. Couples with diazotised bases.
1:5:7	From 1-amino-5-naphthol-7-sulphonic acid by the bisulphite reaction (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii], 80, 239).	Acid, scales, crystallises with $\frac{1}{2}$ mol. of alcohol. Couples with diazotised bases.
1:6:3	(1) Fusion of naphthalene-1:3:6-trisulphonic acid with 90% caustic soda at 250° (Aktienges., G.P. 42261; Bayer, G.P. 63015; cf. Kalle, G.P. 89061). (2) 1-Amino-6-naphthol-3-sulphonic acid heated with water at 200° (Cassella, G.P.a. 5020). (3) From 2-amino-5-naphthol-7-sulphonic acid by the bisulphite reaction (Badische, G.P. 126136; B.P. 1387, 1900; Bucherer, J. pr. Chem. 1904, [ii], 69, 83).	Sodium salt, sparingly soluble, shows in alkaline solution reddish-blue fluorescence. Gives green coloration with ferric chloride. Forms a yellow easily soluble nitroso-compound (Cassella, <i>l.c.</i> ). Couples with diazotised bases (Bayer, G.P. 85241; B.P. 3580, 1895; Cassella, <i>l.c.</i> ).
1:6:4	Fusion of $\alpha$ -naphthylamine-4:6-disulphonic acid (Dahl, G.P. 57114; B.P. 735, 1890); or of $\alpha$ -chloronaphthalene-4:6-disulphonic acid with caustic soda at 210–220° (Rudolph, G.P. 104902).	Acid and acid sodium salt, sparingly soluble leaflets; alkaline solutions show violet fluorescence. Forms a sparingly soluble yellow nitroso derivative (Rudolph, <i>l.c.</i> ). Gives green coloration with ferric chloride. Couples with diazotised bases (Dahl, <i>l.c.</i> ).

## DIHYDROXYNAPHTHALENEMONOSULPHONIC ACIDS—continued.

Constitution.	Preparation.	Acids, salts, and reactions.
O:O:5 1:6:5	From 2-amino-5-naphthol-1-sulphonic acid by the bisulphite method (Bucherer and Wahl, J. pr. Chem. 1921, [ii], 103, 253).	-
1:7:3	(1) Fusion of $\beta$ -naphthol-6:8-disulphonic acid with caustic soda at 220–230° (Höchst, G.P.a. 4153; B.P. 9642, 1889; cf. Bayer, G.P. 85241). (2) Digestion of 2-amino-8-naphthol-6-sulphonic acid with water under pressure (Leman, Bull. Soc. chim. 1941, [v], 8, 576).	<i>Acid sodium</i> salt, readily soluble needles; alkaline solutions show blue fluorescence. Gives green coloration with ferric chloride. Couples with diazotised bases; with tetrazotised bases it gives disazo-dyes (I.G., B.P. 342807. For preparation of esters, see I.G., B.P. 353578).
1:7:4	(1) Fusion of 2-carboxy- $\alpha$ -naphthol-4:7-disulphonic acid with caustic alkali at 230–290° (Bindsch., G.P. 81938; B.P. 4629, 1894). (2) 1:7-Dihydroxy-2-carboxynaphthalene-4-sulphonic acid heated with 30% caustic soda under pressure at 140–160° (Bindsch., G.P. 83965).	<i>Acid</i> and <i>acid</i> salts, readily soluble; alkaline solutions show violet fluorescence. Gives green coloration with ferric chloride. Couples with diazotised bases.
1:8:2	1-Amino-8-naphthol-7-sulphonic acid heated with lime and water under pressure at 250° (Bayer, G.P.a. 7509).	<i>Acid sodium</i> salt, needles, shows reddish-violet fluorescence in solution. Gives green coloration with ferric chloride. Couples with diazotised bases.
1:8:3	(1) $\alpha$ -Naphthylamine-3:8-disulphonic acid heated with 9% caustic soda under pressure at 220–250° (Höchst, G.P.a. 7112). (2) Digestion of $\alpha$ -naphthol-3:8-disulphonic acid or of $\alpha$ -naphthol-6:8-disulphonic acid with 50% caustic soda at 170–210° (Kalle, G.P. 82422). (3) 1-Amino-8-naphthol-3:5-disulphonic acid heated with water at 200° (Leonhardt, G.P.a. 8628; B.P. 19253, 1895; Cassella, G.P. 103848).	<i>Acid sodium</i> salt, sparingly soluble needles; alkaline solutions show blue fluorescence (Kalle, l.c.). Gives green coloration with ferric chloride (Kalle, l.c.). Couples with diazotised bases (cf. Bayer, G.P. 85241).
1:8:4	(1) Fusion of the following with caustic alkali or caustic alkali solution: $\alpha$ -naphthol-4:8-disulphonic acid (Bayer, G.P. 54116; 67829; B.P. 13665, 18517, 1889) or $\alpha$ -naphthol-5:8-disulphonic acid, or its sultone (Bayer, G.P. 80667; B.P. 1227, 1894); also of $\alpha$ -naphthylamine-4:8-disulphonic acid (Bayer, G.P. 71836; Badische, G.P. 91855; B.P. 9894, 1893); or $\alpha$ -naphthylamine-5:8-disulphonic acid (Bayer, G.P. 77285; B.P. 1227, 1894); also of 1-amino-8-naphthol-4-sulphonic acid (Bayer, G.P. 75319; 80315); or 1-amino-8-naphthol-5-sulphonic acid (Bayer, G.P. 75055; B.P. 15269, 1893). (2) 1:8-Diaminonaphthalene-4-sulphonic acid heated with milk of lime at 230° (Cassella, G.P. 75962). (3) From 1-amino-8-naphthol-4-sulphonic acid (Bayer, G.P. 109102; B.P. 16807, 1899), or 5-sulphonic acid (Bucherer, J. pr. Chem. 1904, [iii], 69, 86) by the bisulphite reaction.	<i>Acid</i> forms three series of salts, all easily soluble; <i>monosodium</i> salt, $\text{NaH}_2\text{A}$ , silky leaflets; <i>disodium</i> salt, $\text{Na}_2\text{HA} + 2\text{H}_2\text{O}$ , leaflets; <i>monobarium</i> salt, $\text{BaH}_2\text{A}_2$ , needles; <i>dibarium</i> salt, $\text{BaHA} + \frac{1}{2}\text{H}_2\text{O}$ (Bayer, G.P. 67829; B.P. 13665, 1889). Basic salts (trisodium, etc.) show bluish-green fluorescence in solution. Gives dirty green precipitate with ferric chloride. Couples with diazotised bases, giving azo-dyes which have the property of forming lakes with chromium and other oxides (cf. Bayer, G.P. 61707; 67829; 66693; B.P. 5984, 1891). For monoalkyl derivatives and for azo-dyes obtained by coupling them with diazotised bases, cf. Bayer, G.P. 73741; 78937; B.P. 3495, 1893.
2:3:6	Fusion of $\beta$ -naphthol-3:6-disulphonic acid with caustic soda at 240–280° (Badische, G.P. 57525; B.P. 15803, 1890; Höchst, G.P.a. 4153; B.P. 9642, 1889; Friedländer and Zakrzewski, Ber. 1894, 27, 762).	<i>Acid sodium</i> salt, sparingly soluble leaflets, shows reddish-blue fluorescence in alkaline solution; <i>barium</i> salt, $\text{BaA}_2$ , sparingly soluble (cf. Bayer, G.P. 85241). Gives intense violet coloration with ferric chloride. Couples with diazotised bases, giving azo-dyes which form lakes with metallic oxides (cf. Bayer, G.P. 82774).
2:6:4	The acid described as 2:6-dihydroxynaphthalene-4-sulphonic acid (Bayer, G.P. 72222) is considered by Jacchia to be a disulphonic acid (Annalen, 1902, 323, 131).	
2:7:3	Fusion of $\beta$ -naphthol-3:7-disulphonic acid with caustic alkali (cf. Aktienges., G.P. 63956; Bayer, G.P. 85241).	<i>Sodium</i> salt, sparingly soluble crystalline powder, shows bluish-violet fluorescence in solution. Gives deep blue coloration with ferric chloride.

## DIHYDROXYNAPHTHALENEDISULPHONIC ACIDS.

Constitution.	Preparation.	Acids, salts, and reactions.
O.O:S:5 1:2:3:6 and 1:2:6:8	<p>(1) Acid sodium salt of 1-amino-2-naphthol-3:6-(resp. 6:8)-disulphonic acid boiled with water (Wlitt, Ber. 1888, 21, 3480; G.P. 49857).</p> <p>(2) Reduction of [<math>\beta</math>-naphthaquinone-3:6-(resp. 6:8)-disulphonic acid with sulphurous acid (Witt, <i>ibid.</i> 1891, 24, 3157).</p> <p>(3) 1:2-Dihydroxynaphthalene-3:6-disulphonic acid is also formed when 1:2-diaminonaphthalene-3:6-disulphonic acid is heated with dilute mineral acids (cf. Cassella, G.P. 72584).</p>	<p>Acid sodium salts, readily soluble leaflets; decompose very rapidly in alkaline solution (cf. Bayer, G.P. 79054).</p> <p>Do not couple with diazotised bases (Bayer, <i>l.c.</i>; cf. Wlitt, Ber. 1891, 24, 3156).</p> <p>Precipitate gelatine or basic aniline dyes from solution (Naphthattannins; cf. Wlitt, G.P. 49857).</p>
1:3:5:7	<p>(1) Mixed with 30% of 1:5:3:7- by heating naphthalene 1:3:5:7-tetrasulphonic acid or <math>\alpha</math>-naphthol-3:5:7-trisulphonic acid with 60% caustic soda at 180-200° (Bayer, G.P. 79054; 80464; B.P. 25074, 1893).</p> <p>(2) 2-Amino-4-naphthol-6:8-disulphonic acid heated with water under pressure at 210-220° (Bayer, G.P. 89242).</p>	<p>Sodium salt, readily soluble; potassium salt, leaflets; alkaline solutions show green fluorescence; barium salt, BaA, moderately soluble needles (Friedländer and Rüdtt, Ber. 1890, 29, 1613).</p> <p>Gives blue coloration with ferric chloride.</p> <p>Couples in alkaline solution with diazotised bases, giving <i>azo-dyes</i> of yellow shade (cf. Bayer, G.P. 78877; B.P. 3032, 1894).</p>
1:5:3:7	<p>(1) <math>\alpha</math>-Naphthol-3:5:7-trisulphonic acid heated with 50% caustic soda at 150-160° (Kalle, G.P.a. 12732).</p> <p>(2) Mixed with 70% of 1:3:5:7- from naphthalene-1:3:5:7-tetrasulphonic acid and 60% caustic soda at 180-200°.</p>	<p>Potassium and sodium salts, readily soluble needles; in alkaline solution show bluish-violet fluorescence (Bayer, G.P. 79054).</p> <p>Gives bluish-green coloration with ferric chloride.</p> <p>Couples in acid or alkaline solution (cf. Bayer, <i>l.c.</i>) with 1 or 2 mol. (cf. Kalle, <i>l.c.</i>) of diazotised bases, giving <i>azo-dyes</i>.</p>
1:5:(2):(4)	1:5-Dihydroxynaphthalene sulphonated with sulphuric acid at 100-160° or with naphthoic acid in the cold (Ewer and Pick, G.P. 41934).	No description published, but acid said to couple with diazotised bases (Ewer and Pick, <i>l.c.</i> ; cf. 2- and 4-monosulphonic acids).
1:(7):(2):(4)	Fusion of $\alpha$ -naphthol-2:4:7-trisulphonic acid with caustic alkali (cf. Höchst, G.P. 67426; B.P. 18783, 1891).	No description published.
1:7:3:6	Mixed with 30% of the 2:3:6:8-acid, by fusion of $\beta$ -naphthol-3:6:8-trisulphonic acid with caustic alkali at 230-240° (Höchst, G.P.a. 4154; B.P. 9642, 1889; G.P. 67503; cf. Friedländer and Silberstein, Monatsh. 1902, 23, 527).	<p>Sodium salt, Na<sub>2</sub>A, sparingly soluble needles; alkaline solutions show bluish-green fluorescence.</p> <p>Forms a dark blue precipitate with formaldehyde and hydrochloric acid (Friedländer and Silberstein, <i>l.c.</i>).</p> <p>Gives fleeting blue coloration with ferric chloride (<i>ibid.</i>).</p> <p>Couples with diazotised bases (Höchst, <i>l.c.</i>).</p>
1:8:2:4	<p>(1) 1-Amino-8-naphthol- or naphthasultam-2:4-disulphonic acid heated with 80% caustic soda solution at 250° (Bayer, G.P. 77703; B.P. 4979, 1893; Cassella, G.P. 81282, Dressel and Kothe, Ber. 1894, 27, 2142).</p> <p>(2) 1-Amino-8-naphthol-5:7-disulphonic acid heated with dilute caustic soda solution above 250° (Badische, G.P.a. 16142; B.P. 18924, 1893).</p> <p>(3) Fusion of <math>\alpha</math>-naphthol-2:4:8-trisulphonic acid with caustic alkali at 210° (Bayer, G.P. 57021; B.P. 3397, 1890; Dressel and Kothe, Ber. 1894, 27, 2144).</p>	<p>Disodium salt, readily soluble needles, showing faint blue fluorescence in solution; trisodium salt, Na<sub>3</sub>HA+4H<sub>2</sub>O, readily soluble prisms, formed in alkaline solution shows greenish fluorescence (Dressel and Kothe, <i>l.c.</i>).</p> <p>Forms a soluble orange mononitroso-compound (Cassella, <i>l.c.</i>; Dressel and Kothe, <i>l.c.</i>).</p> <p>Gives green coloration with ferric chloride (cf. Badische, <i>l.c.</i>).</p> <p>Couples with diazotised bases (cf. Bayer, G.P. 73551; B.P. 18517, 1889).</p> <p>In acid solution with dichromate gives black dye on wool (Cassella, <i>l.c.</i>).</p>
1:8:3:5	<p>(1) Fusion of <math>\alpha</math>-naphthol-4:6:8-trisulphonic acid with 70% caustic soda solution under pressure at 170-190° (Bayer, G.P.a. 7004; B.P. 171410, 1893; cf. Kalle, B.P. 1641, 1894).</p> <p>(2) 1-Amino-8-naphthol-3:5-disulphonic acid heated with 7% caustic soda solution under pressure at 240° (Leonhardt, G.P.a. 8682; B.P. 21919, 1895; Cassella, G.P. 108848).</p> <p>(3) 1-Amino-8-naphthol-4:6-disulphonic acid heated with 70% caustic alkali solution above 240° (Bayer, G.P. 80741; B.P. 171410, 1893).</p>	<p>Disodium salt readily soluble needles; solutions of acid salts show faint blue fluorescence (cf. Bayer, G.P. 79054).</p> <p>Forms a readily soluble yellow nitroso derivative.</p> <p>Gives green coloration with ferric chloride (Bayer, <i>l.c.</i>).</p> <p>Couples with diazotised bases (Bayer, G.P.a. 7004; B.P. 171410, 1893).</p>

Constitution.	Preparation.	Acids, salts, and reactions.
O:O:S:5 1:8:3:6 Chromotrope acid.	(1) $\alpha$ -Naphthol-3:6:8-trisulphonic acid or its sultone heated with 60% caustic soda at 170–220° (Höchst, G.P. 67563). (2) 1-Amino-8-naphthol-3:6-disulphonic acid heated with 5% caustic soda under pressure at 265° (Bayer, G.P. 68721; B.P. 11522, 1892). (3) 1:8-Diaminonaphthalene-3:6-disulphonic acid heated with 5% caustic soda under pressure at 260–280° (Bayer, G.P. 69190; B.P. 11522, 1892), or with dilute mineral acids or water under pressure at 150–160° (Cassella, G.P. 75153; cf. Voroschov and Jurigina, Anilinokras. Prom. 1933, 3, 453; B. 1934, 393). (4) 8-Chloro- $\alpha$ -naphthol-3:6-disulphonic acid fused with caustic alkali (Badische, G.P. 147852).	Acid forms four series of salts, two strongly acid, one neutral, one basic. <i>Disodium</i> salt, $\text{Na}_2\text{H}_2\text{A} + 2\text{H}_2\text{O}$ , readily soluble in water, and acid towards sodium carbonate; alkaline solutions show violet-blue fluorescence. <i>Barium</i> salt, $\text{BaH}_2\text{A} + 3\text{H}_2\text{O}$ , small leaflets, which in solution with sodium carbonate yields the <i>sodium barium</i> salt, $\text{BaNaHA} + 3\text{H}_2\text{O}$ , needles (Höchst, l.c.). Gives grass-green coloration with ferric chloride. With oxidising agents gives <i>juglone</i> -2:7-disulphonic acid (Rosenhauer, Wirth, and Königer, Ber. 1929, 62 [B], 2717). Couples with 1 or 2 mol. of diazotised bases, giving <i>ortho</i> -azo-dyes (Hantower and Tauber, Ber. 1898, 31, 2156) which form lakes with chromium salts (cf. Höchst, G.P. 59161). In acid solution with dichromate gives brown dye on wool (Höchst, G.P. 77552). For <i>monoalkyl</i> derivatives, cf. Bayer, G.P. 73251; 73741; B.P. 3493, 1893. For <i>chloro</i> derivative and derived azo-dyes, cf. Höchst, G.P. 153195).
1:8:?:?	1:8-Dihydroxynaphthalene sulphonated with sulphuric acid at 50° and the three products separated by means of their barium salts (Badische, B.P. 14294, 1891; G.P. 79029, 79030).	<i>Sodium</i> salts very readily soluble, show blue fluorescence in alkaline solution. Give green colorations with ferric chloride. Couple with diazotised bases, forming azo-dyes (cf. Bayer, G.P. 79054).
2:3:6:8	Mixed with the 1:7:3:6-acid by fusion of $\beta$ -naphthol-3:6:8-trisulphonic acid with caustic alkali and separation from the less soluble isomer by fractional precipitation with brine (Höchst, G.P. 67563; cf. Friedländer and Silberstern, Monatsh. 1902, 23, 527).	<i>Sodium</i> salt, $\text{Na}_2\text{A} + 3\frac{1}{2}\text{H}_2\text{O}$ , easily soluble needles, shows bluish-violet fluorescence in alkaline solution; <i>barium</i> salt, $\text{BaA}$ , sparingly soluble needles. Gives violet coloration with ferric chloride, but no precipitate with formaldehyde and hydrochloric acid (Friedländer and Silberstern, l.c.). Couples with diazotised bases ( <i>idem</i> , <i>ibid.</i> ).
2:7:3:6	(1) 2:7-Dihydroxynaphthalene sulphonated with sulphuric acid on a water bath (Aktenges., G.P. 75142; B.P. 16199, 1893). (2) $\beta$ -Naphthol-3:6:7-trisulphonic acid heated with 66% caustic soda solution under pressure at 220–300° (Bayer, G.P.a. 7243; B.P. 250744, 1893).	<i>Acid sodium</i> salt moderately soluble; <i>potassium</i> salt, large needles; <i>barium</i> salt, almost insoluble; salts show bluish-green fluorescence in alkaline solution (cf. Bayer, G.P. 79054). Forms a sparingly soluble orange <i>nitroso</i> -compound. Gives deep blue coloration with ferric chloride. Couples in alkaline solution with 1 mol. of diazotised bases (Bayer, G.P.a. 7243).

## AMINODIHYDROXYNAPHTHALENES.

The aminodihydroxynaphthalenes are little known and have no technical value. Their properties are summarised below:

N:O:O ( $\text{NH}_2\cdot\text{C}_{10}\text{H}_7(\text{OH})_2$ ).

1:2:3 Decomposes at 230° (Friedländer and Silberstern, Monatsh. 1902, 23, 521).

1:2:4 Isolation doubtful. *Triacetyl* derivative, tablets, m.p. 155–156° (Kehrmann and Hertz, Ber. 1896, 29, 1419). An amino-1:3-dihydroxynaphthalene, which may have this constitution, has been described by Zincke and Wiegand (Annalen, 1895, 286, 89) (cf. Friedländer and Rüdert (Ber. 1896, 29, 1611)).

1:2:6 Not isolated. Obtained by reduction of azo derivative of 2:6-dihydroxynaphthalene (Kehrmann, *ibid.* 1907, 40, 1962). The 4-sulphonic acid is obtained by reduction of 1-nitroso-2:6-dihydroxynaphthalene with sodium bisulphite solution (Bayer, G.P. 87900; B.P. 6035, 1893).

1:2:7 Not isolated. Obtained by reduction of nitroso-2:7-dihydroxynaphthalene (Clausius, Ber. 1890, 23, 521). *Triacetyl* derivative m.p. 183° (Nietzki and Knapp, *ibid.* 1897, 30, 1123). 7-Methyl ether, leaflets, m.p. 170°; 2:7-dimethyl ether, needles, m.p. 82–83° (Fischer and Kern, J. pr. Chem. 1913, [iii], 94, 26).

## N:O:O

The 4-sulphonic acid is obtained by reduction of 1-nitroso-2:7-dihydroxynaphthalene with sodium bisulphite.

1:3:4 Not isolated. *Triacetyl* derivative, prisms, m.p. 193° (Kehrmann, Ber. 1894, 27, 3340).

1:4:7 Easily oxidisable (Fischer and Bauer, J. pr. Chem. 1916, [iii], 94, 7).

1:5:8 Not isolated. *Triacetyl* derivative, needles, m.p. 165° (Graebe and Oeser, Annalen, 1904, 335, 149).

1(6):8 Unknown. The (3)-sulphonic acid, obtained by fusing 1-amino-8-naphthol-3:6-disulphonic acid with 60% caustic soda at 210° is diazotisable (Bayer, G.P. 75097).

2:1:4 Not isolated. *Triacetyl* derivative, needles, m.p. 259–260° (Kehrmann, Ber. 1894, 27, 3343).

2:1:5 Stellate groups (Fischer and Bauer, J. pr. Chem. 1917, [ii], 95, 262). Very sensitive to light.

2:1:6 Unstable. *Triacetyl* derivative, needles, m.p. 150° (Fischer and Bauer, *ibid.* 1916, [iii], 94, 5).

2:3:4 Needles, m.p. 164°. *Triacetyl* derivative, needles, decomp. above 200° (Zincke and Noack, Annalen, 1897, 295, 13).

2(3):8 Unknown. The (6)-sulphonic acid obtained by fusing 2-amino-8-naphthol-3:6-disulphonic acid with caustic alkali at 240–280°, is diazotisable (Höchst, G.P. 53023; B.P. 15175, 1899).

## DIAMINODIHYDROXYNAPHTHALENES.

Several diaminodihydroxynaphthalenes have been described, chiefly the products of reduction of disazo-dyes obtained from dihydroxynaphthalenes.

1:4-Diamino-2:3-dihydroxynaphthalene is obtained by reduction of the disazo-dyes from 2:3-dihydroxynaphthalene. It forms a *sulphate*,  $\text{B}_2\text{H}_2\text{SO}_4$ , leaflets, and gives *isonaphthazarin* with ferric chloride (Friedländer and Silberstern, *Monatsh.* 1902, 23, 524).

1:6-Diamino-4:5-dihydroxynaphthalene, obtained by reduction of the disazo-dyes from 1:8-dihydroxynaphthalene, is very rapidly oxidised.

1:8-Diamino-2:7-dihydroxynaphthalene is obtained by reduction of the disazo-dyes from 2:7-dihydroxynaphthalene. It gives a *sulphate*, needles, which forms a blue solution in alkalis (Cassella, G.P. 108166; B.P. 9502, 1899).

## TRIHYDROXYNAPHTHALENES.

The trihydroxynaphthalenes have little technical interest. They are produced by fusion of naphthalene- or naphthol-sulphonic acids with caustic alkali, or by reduction of hydroxynaphthoquinones, but the number of isomers thus furnished is limited by the small number of acids or quinones available. Only six of the fourteen possible isomers have been isolated and characterised, but sulphonic acids of two others are known.

(i) 1:2:3-Trihydroxynaphthalene (*Naphthapyrogallol*) is obtained by reduction of *isonaphthazarin* with zinc and boiling dilute sulphuric acid (Zincke and Ossenbeck, *Annalen*, 1899, 307, 18). It is crystalline and gives a *triacetate*, in prisms, m.p. 250–255° (Zincke and Noack, *ibid.* 1897, 295, 19).

(ii) 1:2:4-Trihydroxynaphthalene is obtained by reduction of hydroxy-[ $\alpha$ ]naphthoquinone with tin and hydrochloric acid, or from its *triacetate* by hydrolysis with alcoholic hydrogen chloride (Thiele and Winter, *ibid.* 1900, 311, 346; G.P. 101607; B.P. 10590, 1898). It crystallises in needles, m.p. 154°. In alkaline solution it is readily oxidised by air to hydroxy-[ $\alpha$ ]naphthoquinone.

The *triacetate*, obtained by heating [ $\alpha$ ] or [ $\beta$ ]naphthoquinone and acetic anhydride with a small quantity of sulphuric acid, or phosphoric acid (Bayer, G.P. 107508) at 30–40°, or with zinc chloride at 50–60°, crystallises in needles, m.p. 134–135°.

(iii) 1:3:5-Trihydroxynaphthalene. — The 7-sulphonic acid is formed when naphthalene-1:3:5:7-tetrasulphonic acid or  $\alpha$ -naphthol-3:5:7-trisulphonic acid or the 1:3- or 1:5-dihydroxydisulphonic acid is fused with caustic potash at 280° (Bayer, G.P. 80464; B.P. 19624, 1893). Its *potassium* salt forms needle crystals and couples with 1 or 2 mol. of a diazotised base, forming azo-dyes (Bayer, G.P. 87583; B.P. 1229, 1894).

(iv) 1:3:6-Trihydroxynaphthalene is obtained by fusing 1:6-dihydroxynaphthalene-3-sulphonic acid with caustic soda at 250–270° (Meyer and Hartmann, *Ber.* 1905, 38, 3950). It forms doubly refracting crystals, m.p. 95°, a

*hydrochloride* in yellow needles, and a *triacetate*, needles, m.p. 112–113°. On boiling the aqueous solution a *polymer*,  $\text{C}_{20}\text{H}_{10}(\text{OH})_6$ , possibly a dinaphthyl derivative, is formed, of which the *hexa-acetate*, scales, has m.p. 200°. It couples with 1 or 2 mol. of diazotised bases forming azo-dyes (Bayer, G.P. 78604).

(v) 1:4:5-Trihydroxynaphthalene ([ $\alpha$ ]-*hydrojuglone*), mixed with about one-fifth the amount of [ $\beta$ ]-*hydrojuglone*, is present in the shell of the walnut. It is insoluble in chloroform; the [ $\beta$ ] form is easily soluble (Mylus, *Ber.* 1884, 17, 2412; 1885, 18, 2568). On melting, the [ $\alpha$ ] compound gives an equilibrium mixture containing about 75% of the [ $\beta$ ] form, whilst an alkaline solution of the latter regenerates the [ $\alpha$ ] compound on acidification, the isomerism being keto-enolic (Willstätter and Wheeler, *ibid.* 1914, 47, 2796). The [ $\alpha$ ] compound separates from water in scales or needles, m.p. 148°.

The 8-chloro derivative, m.p. 115–120° (decomp.), may be obtained from 1:5-dihydroxynaphthalene by chlorination of the diacetate at 80°, oxidation of the product to 8-chloro-5-acetoxy-[ $\alpha$ ]naphthoquinone, m.p. 143°, hydrolysis and reduction (Wheeler and Mattox, *J. Amer. Chem. Soc.* 1933, 55, 686). The 2:6-dibromo derivative is similarly obtained (Wheeler and Ergle, *ibid.* 1930, 52, 4872).

The trihydroxynaphthalene with ferric chloride gives juglone. With acetic anhydride it yields the *triacetate* of the [ $\beta$ ] form in prisms, m.p. 129–130°. [ $\beta$ ]-*Hydrojuglone* crystallises in hexagonal tablets, m.p. 96–97°.

(vi) 1:4:6-Trihydroxynaphthalene is obtained by reducing 6-hydroxy- $\alpha$ -naphthoquinone with stannous chloride. It forms star-like groups of needles, m.p. 138–140°. It is unstable in air, being readily oxidised. The *triacetate*, needles, has m.p. 94–95° (Fischer and Bauer, *J. pr. Chem.* 1916, [ii], 94, 8).

(vii) 1:6:7-Trihydroxynaphthalene is obtained by heating 1:6:7-trihydroxynaphthalene-3-sulphonic acid with water or 5% sulphuric acid under pressure at 210–220° (Friedländer and Silberstern, *Monatsh.* 1902, 23, 530). It forms needles, m.p. 175°, a *triacetate*, needles, m.p. 143–144°, and a *trimethyl ether*, prisms, m.p. 127–128°. It couples in the 4-position with 1 mol. of a diazotised base, giving azo-dyes which form lakes with chromium or iron salts (Cassella, G.P. 110618; 110904).

The 3-sulphonic acid may be prepared from  $\beta$ -naphthol-3:6:8-trisulphonic acid by prolonged fusion with caustic soda at 240–250°. Its *barium salt*,  $\text{BaA}_3$ , forms sparingly soluble leaflets, its *sodium salt* sparingly soluble needles. With formaldehyde and hydrochloric acid it gives a violet precipitate. With diazotised bases it couples, forming azo-dyes (cf. Höchst, G.P. 67426; B.P. 18783, 1891).

## TETRAHYDROXYNAPHTHALENES.

(i) 1:2:3:4-Tetrahydroxynaphthalene (*Leucoisonaphthazarin*) is obtained from *isonaphthazarin* by reduction. It forms easily soluble scales, and its *tetra-acetyl* derivative, needles, has m.p. 220°. It is readily oxidised to *isonaphthazarin*, or reduced to 1:2:3-trihydroxy-

naphthalene (Zincke and Ossenbeck, *Annalen*, 1899, 307, 16).

(ii) 1:4:5:6-Tetrahydroxynaphthalene is obtained from 6-hydroxy-[ $\alpha$ ]naphthaquinone by nitration to the 5-nitro derivative, reduction with stannous chloride to 5-amino-1:4:6-trihydroxynaphthalene, oxidation by ferric chloride to 5:6-dihydroxy-[ $\alpha$ ]naphthaquinone and finally reduction with stannous chloride to the tetrahydroxy derivative. It crystallises in needles, m.p. 180° (decomp.); its *tetra-acetate*, in prisms, has m.p. 202°. When oxidised by manganese dioxide and sulphuric acid it yields a *naphthapurpurin* identical with that from naphthazarin (Dimroth and Roos, *ibid.* 1927, 456, 187).

(iii) 1:4:5:8-Tetrahydroxynaphthalene is obtained by reduction of naphthazarin (v. p. 384b) with zinc dust and dilute sulphuric acid (Zahn and Ochwat, *ibid.* 1928, 462, 82); or by action of iron on a boiling aqueous "naphthazarin melt" (Badische, G.P. 129074; B.P. 23887, 1900). It forms needles, m.p. 190°, and its *tetra-acetyl* derivative, minute prisms, has m.p. 277-279° (Liebemann, *Ber.* 1895, 28, 1457; Wheeler and Edwards, *J. Amer. Chem. Soc.* 1916, 38, 387). It is easily soluble in alcohol, ether, and acetic acid. The alcoholic solution shows a violet fluorescence. It is very rapidly oxidised by air. It is readily oxidised to naphthazarin and is a substantive dye which, when oxidised with chromic acid, on the fibre, gives black shades. The same structure has been claimed for a poly-hydroxynaphthalene, m.p. 224°, which results from reduction of 2:3:8-tribromojuglone (Wheeler and Andrews, *ibid.* 1921, 43, 2584).

### MERCAPTANS AND SULPHIDES.

Apart from sulphonic acids, sulphur-containing derivatives of naphthalene are of minor importance. Some mercapto-compounds are intermediates in the manufacture of vat dyestuffs. The preparation of sulphur derivatives of naphthalene is carried out by:

1. Reduction of the corresponding sulphonyl chlorides to mercaptans.
2. Reaction of a diazo-compound with sodium disulphide or xanthate leading eventually to the disulphide and by reduction to the mercaptan.
3. Direct reaction with sulphur to give mono-, di-, and poly-sulphides (of particular application to the naphthols).
4. Reaction of carbon disulphide and sulphur with naphthylamines to give a mercapto-naphthothiazole which is subsequently hydrolysed to the aminonaphthylmercaptan.

#### MERCAPTANS.

$\alpha$ -Naphthylmercaptan (*thio- $\alpha$ -naphthol*) is obtained by reduction of naphthalene- $\alpha$ -sulphonyl chloride by zinc and dilute sulphuric acid (Bourgeois, *Rec. trav. chim.* 1899, 18, 441) or by electrolytic reduction (Fichter and Tamm, *Ber.* 1910, 43, 3033). An alternative method is by the action of diazotised  $\alpha$ -naphthylamine on potassium xanthate followed by hydrolysis and

reduction (Leuckart, *J. pr. Chem.* 1890, [ii], 41, 216); or diazotised  $\alpha$ -naphthylamine-8-sulphonic acid with sodium disulphide is converted into dinaphthylsulphidedisulphonic acid which is hydrolysed to dinaphthylsulphide and then reduced to  $\alpha$ -naphthylmercaptan (I.G., G.P. 433103). It is a liquid, b.p. 161°/20 mm., volatile in steam but decomposing under ordinary pressure when heated to 285° giving 1:1'-dinaphthylsulphide and  $H_2S$  (Leuckart, *l.c.*). It is soluble in alcohol and ether but only sparingly so in aqueous alkalis. It is oxidised by air in the presence of alkali to 1:1'-dinaphthylsulphide (Leuckart, *l.c.*). It has been proposed as a plasticising agent for rubber (Du Pont, B.P. 490292). With oxalyl chloride it gives  *$\alpha$ -naphthathiofuran-1:2-dione* (Gesellsch., Swiss. P. 100851).

4-Amino- $\alpha$ -naphthylmercaptan, m.p. 91-93°, is prepared from naphthionic acid by acetylation and interaction with phosphorus pentachloride to give 4-acetamidonaphthalene-1-sulphonyl chloride which is reduced by zinc dust to 4-acetamido- $\alpha$ -naphthylmercaptan and finally hydrolysed (Zincke and Schutz, *Ber.* 1912, 45, 473).

4-Hydroxy- $\alpha$ -naphthylmercaptan, m.p. 114°, is prepared from  $\alpha$ -naphthol-4-sulphonic acid, the hydroxyl group being protected by interaction with ethyl chloroformate, converted to sulphonyl chloride, and the product reduced and hydrolysed (Zincke and Ruppersberg, *ibid.* 1915, 48, 120). 5-Hydroxy- $\alpha$ -naphthylmercaptan, m.p. 131-132°, is similarly prepared from  $\alpha$ -naphthol-5-sulphonic acid (Rennert, *ibid.* 1915, 48, 459).

$\beta$ -Naphthylmercaptan (*thio- $\beta$ -naphthol*) is prepared by reduction of naphthalene- $\beta$ -sulphonyl chloride with zinc and acid (Bourgeois, *Rec. trav. chim.* 1899, 18, 441) or from  $\beta$ -naphthylamine-1-sulphonic acid by diazotisation and reaction with sodium disulphide to give the corresponding dinaphthylsulphidedisulphonic acid which is hydrolysed to 2:2'-dinaphthylsulphide and then reduced to  $\beta$ -naphthylmercaptan (I.G., G.P. 433103). It has m.p. 81°, b.p. 288°, and is only slightly volatile in steam. On distillation there is partial decomposition to 2:2'-dinaphthylsulphide and  $H_2S$ . It is readily oxidised by air in the presence of alkali to 2:2'-dinaphthylsulphide. It is claimed as a plasticising agent in the milling of rubber (Du Pont, B.P. 490292).

6-Hydroxy- $\beta$ -naphthylmercaptan, m.p. 137°, is prepared as described for 4-hydroxy- $\alpha$ -naphthylmercaptan (Zincke and Dereser, *Ber.* 1918, 51, 352).

1-Amino- $\beta$ -naphthylmercaptan is prepared by interaction of carbon disulphide and sulphur with  $\alpha$ -naphthylamine to give 2-mercapto-2':1'-naphthothiazole which is hydrolysed with aqueous caustic soda. It is an intermediate for the preparation of thioindigoid dyes.

#### DINAPHTHYLSULPHIDES AND DISULPHIDES.

1:1'-Dinaphthylsulphide, m.p. 110°, is obtained by distillation of naphthalene- $\alpha$ -sulphonate with potassium thiocyanate (Arm-

strong, *ibid.* 1874, 7, 407), by elimination of  $\text{H}_2\text{S}$  in the distillation of  $\alpha$ -naphthylmercaptan at ordinary pressure (Leuckart, J. pr. Chem. 1890, [ii], 41, 217) or by distillation of the lead salt of  $\alpha$ -naphthylmercaptan under reduced pressure (Krafft and Schönherr, Ber. 1889, 22, 823).

2:2'-Dihydroxy-1:1'-dinaphthylsulphide is obtained by heating  $\beta$ -naphthol in dilute aqueous caustic soda with excess of sulphur (Henriques, *l.c.*). It is also obtained by heating  $\beta$ -naphthol with sulphur alone or in solvent with gradual addition of lead oxide (Dahl, G.P. 35788; Ullmann and Bühler, J.C.S. 1906, 90, [i], 44) or by interaction of 1-chloro- $\beta$ -naphthol with sodium sulphide (Ringissen, Compt. rend. 1934, 198, 2180). 2:2'-Dihydroxydinaphthylsulphide ( $\beta$ -naphthol sulphide), first studied in detail by Henriques (*ibid.* 1894, 27, 2999), apparently existed in two forms which were considered to be stereoisomers but later work by Smiles and collaborators (J.C.S. 1912, 101, 1146, 1423; 1914, 105, 1750; 1930, 956; 1931, 914) showed that the so-called *iso*- $\beta$ -naphthol sulphide is a thiol derivative of 1:2'-dinaphthyl ether. This product on heating alone or in a solvent, particularly in an alkaline medium, changes to 2:2'-dihydroxydinaphthylsulphide. It has m.p. 214–215° and couples with diazo-compounds with elimination of sulphur giving azo derivatives of  $\beta$ -naphthol (Henriques, *l.c.*; Porai-Koschitz, G.P. 308909). Interaction with oxalyl chloride converts it into a naphthathiofuran derivative (Gesellschaft, G.P. 402994).

2:2'-Dinaphthylsulphide, m.p. 151°, is obtained by heating the lead salt of  $\beta$ -naphthylmercaptan or by heating 2:2'-dinaphthylsulphide with copper (Krafft and Schönherr, Ber. 1889, 22, 823).

1:1'-Dinaphthylsulphide, m.p. 91°, is obtained by air oxidation of an alkaline solution of  $\alpha$ -naphthylmercaptan (Leuckart, J. pr. Chem. 1890, [ii], 41, 217) or by electrolytic reduction of naphthalene- $\alpha$ -sulphonyl chloride in alcoholic sulphuric acid (Fichter and Tamm, Ber. 1910, 43, 3032) as a stage in the further reduction to  $\alpha$ -naphthylmercaptan. By heating to 260–270° it is converted to a mixture of 1:1'-dinaphthylmonosulphide and 1:1'-dinaphthyltrisulphide (Hinsberg, *ibid.* 1910, 43, 1876).

2:2'-Dihydroxy-1:1'-dinaphthylsulphide is produced by heating  $\beta$ -naphthol with sulphur (Onufrowicz, *ibid.* 1890, 23, 3363) or in admixture with the monosulphide by heating  $\beta$ -naphthol in aqueous alkaline solution with sulphur (Lange, *ibid.* 1888, 21, 261; Henriques, *ibid.* 1894, 27, 2999).

2:2'-Dinaphthylsulphide, m.p. 139°, is obtained by air oxidation of an alkaline solution of  $\beta$ -naphthylmercaptan (Leuckart, *l.c.*) or in admixture with other products by action under pressure of potassium hydrogen sulphide on naphthalene- $\beta$ -sulphonic acid (Schwalbe, *ibid.* 1906, 39, 3104) or by reduction of naphthalene- $\beta$ -sulphonyl chloride with zinc and sulphuric acid (Mackopar, Zeit. für. Chem. 1869, 711). It is readily reduced to  $\beta$ -naphthylmercaptan (Leuckart, *l.c.*); hydrogen peroxide oxidises it to the disulphoxide (Hinsberg, Ber. 1908, 41, 4296).

## ALDEHYDES.

The naphthaldehydes have not achieved any technical importance and consequently there is no extensive literature.

$\alpha$ -Naphthaldehyde is prepared by oxidation of  $\alpha$ -naphthylcarbinol (Bamberger and Lodter, *ibid.* 1888, 21, 259); or from  $\alpha$ -naphthylglyoxylic acid by formation of the anil and subsequent acid hydrolysis (Rousset, Bull. Soc. chim. 1897, [iii], 17, 303); or by distillation of a mixture of calcium  $\alpha$ -naphthoate and calcium formate (Lugli, Gazzetta, 1881, 11, 394). A convenient method of preparation is from  $\alpha$ -chloromethylnaphthalene which with hexamethylenetetramine gives a 60% yield of  $\alpha$ -naphthaldehyde (Coles and Dodds, J. Amer. Chem. Soc. 1938, 60, 853).

*Identification and Reactions.*— $\alpha$ -Naphthaldehyde is a liquid of b.p. 291.6° (Bamberger and Lodter, *l.c.*). The *oxime* has m.p. 98°; *semicarbazone*, m.p. 219°;  $\alpha$ -naphthaldehyde m.p. 156°.

On nitration it yields a mixture of the 5- and 8-nitro derivatives (Ruggli and Burekhardt, Helv. Chim. Acta, 1910, 23, 441). 2-Chloro- $\alpha$ -naphthaldehyde is obtained by hydrolysis of 2-chloro-1-dichloromethylnaphthalene with acetic acid (Sachs and Brigl, Ber. 1911, 44, 2100). 2-Hydroxy- $\alpha$ -naphthaldehyde (m.p. 84°) can be prepared by the action of hydrocyanic acid and zinc chloride on  $\beta$ -naphthol (Gattermann and Horlacher, *ibid.* 1899, 32, 284), but a more recent method is from formamide and  $\beta$ -naphthol in presence of aluminium chloride (I.G., G.P. 519806; cf. Ruggli and Burekhardt, *l.c.*, p. 445); on nitration it yields the 6-nitro-compound. 4-Hydroxy- $\alpha$ -naphthaldehyde has been prepared by Gattermann (*l.c.*) and dihydroxynaphthaldehydes from dihydroxynaphthalenes (Morgan and Vining, J.C.S. 1921, 119, 177; Adams and Burney, J. Amer. Chem. Soc. 1941, 63, 1103). 8-Carboxy- $\alpha$ -naphthaldehyde has been used for preparation of vat dyestuffs (Kalle, G.P. 384982).

$\beta$ -Naphthaldehyde, m.p. 60°, can be prepared in 65% yield by distillation in a vacuum of a mixture of calcium  $\beta$ -naphthoate and calcium formate (Behrend and Ludewig, Annalen, 1911, 379, 352). It has also been prepared by reduction of  $\beta$ -naphthoic acid with sodium amalgam. Fulton and Robinson (J.C.S. 1939, 200) briefly describe the preparation of  $\beta$ -naphthaldehyde and its use in preparation of derivatives. A detailed description of its preparation in 80% yield by catalytic reduction of  $\beta$ -naphthoyl chloride is given by Herschberg and Cason (Organic Syntheses, Vol. XXI, p. 84).

3-Hydroxy- $\beta$ -naphthaldehyde (m.p. 99–100°) has been prepared by hydrogenation of 2-acetoxy-3-naphthoyl chloride to 2-acetoxy-3-naphthaldehyde and subsequent hydrolysis. It is yellow. Its *oxime* has m.p. 207° (decomp.); *phenylhydrazone*, m.p. 248° (Boehn and Profft, Arch. Pharm. 1931, 269, 25). 3-Chloro- $\beta$ -naphthaldehyde, m.p. 121°, has been prepared by hydrogenation of 3-chloro-2-naphthoyl chloride (Shoosmith and Mackie, J.C.S. 1930, 1584).



## CARBOXYLIC ACIDS.

Of the carboxylic derivatives of naphthalene by far the most important is 2-hydroxy-3-naphthoic acid, which is itself used in the manufacture of azo-dyes and pigments, and in the form of its anilide, and substitution products thereof finds extensive application for the production of fast, insoluble azo-dyes on cotton. Many other naphthoic acid derivatives have attracted the attention of dyestuff manufacturers. 8-Amino-1-naphthoic acid is used in the manufacture of vat dyes of the anthanthrone series.

## NAPHTHOIC ACIDS.

$\alpha$ -Naphthoic Acid can be prepared by boiling  $\alpha$ -naphthonitrile with a mixture of sulphuric and acetic acids (Rahe, Ber. 1898, 31, 1898). It is also formed when  $\alpha$ -bromonaphthalene is heated with aqueous potassium cyanide and a small quantity of cuprous cyanide at 200° under pressure (Rosenmund and Struck, *ibid.* 1919, 52 [B], 1755). It is prepared in 68–70% yield by passing carbon dioxide into a well-cooled benzene solution of the Grignard reagent from  $\alpha$ -bromonaphthalene and decomposing the product with sulphuric acid (Gilman, St. John, and Schultze, Organic Syntheses, 1931, Vol. XI, p. 80; cf. Whitmore and Fox, J. Amer. Chem. Soc. 1929, 51, 3363). It crystallises in needles, m.p. 160°, b.p. 300°, dissolves only sparingly in hot water, and on nitration yields both the 5-nitro- and 8-nitro- $\alpha$ -naphthoic acids (Ekstrand, J. pr. Chem. 1888, [ii], 38, 156). The barium salt,  $\text{BaA}_2 + 4\text{H}_2\text{O}$ , and the calcium salt,  $\text{CaA}_2 + 2\text{H}_2\text{O}$ , crystallise in needles. It forms an explosive peroxide (Pummerer *et al.*, Annalen, 1933, 503, 40).

The nitrile, m.p. 34°, b.p. 299°, is obtained from  $\alpha$ -naphthylamine by diazotisation, followed by the Sandmeyer reaction, in which it is an advantage to use potassium nickel cyanide (McRae, J. Amer. Chem. Soc. 1930, 52, 4550). A yield of 92–93% is obtained if  $\alpha$ -chloronaphthalene is heated with cuprous cyanide in pyridine at 220–250° (Newman, *ibid.* 1937, 59, 2472).

In 8-nitro- $\alpha$ -naphthoic acid, the nitro-group is easily replaced by means of sulphuryl chloride, giving 8-chloro- $\alpha$ -naphthoic acid, m.p. 167–168°, but with sulphuryl bromide only 9% of 8-bromo- $\alpha$ -naphthoic acid, m.p. 178°, is obtained (Rule and Barnett, J.C.S. 1932, 175); the latter can be made also from 8-hydroxymercuri- $\alpha$ -naphthoic acid (Corbellini, Swiss. P. 209332; G.P. 684586).

$\beta$ -Naphthoic Acid is obtained when  $\beta$ -naphthonitrile is boiled with alcoholic potash (Vieth, Annalen, 1876, 180, 305), or with a mixture of sulphuric and acetic acids (Baeyer and Besemfelder, *ibid.* 1891, 266, 187). It is obtained in 60% yield from  $\beta$ -bromonaphthalene by the Grignard reaction (Gilman and St. John, Rec. trav. chim. 1929, 48, 743). It crystallises in silky needles, m.p. 184°, dissolves only sparingly in hot water, and yields trimellitic acid on oxidation with alkaline permanganate (Ekstrand, J. pr. Chem. 1891, [ii], 43, 427). The barium salt,  $\text{BaA}_2 + 4\text{H}_2\text{O}$ , and calcium

salt,  $\text{CaA}_2 + 3\text{H}_2\text{O}$ , crystallise in very sparingly soluble needles. The nitrile forms scales, m.p. 66·5°, b.p. 306·5°. The hydrazide has m.p. 147·5° (Goldstein and Cornamúsz, Helv. Chim. Acta, 1932, 15, 939). On reduction with sodium amalgam,  $\beta$ -naphthoic acid forms  $\beta$ -naphthaldehyde (Weil and Ostermeier, Ber. 1921, 54 [B], 3217).

$\beta$ -Naphthoic acid can be sulphonated to give 5-, 7-, and 8-sulphonic acids which in turn can be converted to the corresponding hydroxy derivatives (Royle, Schedler, and Butler, J.C.S. 1923, 123, 1641).

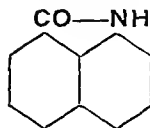
On nitration,  $\beta$ -naphthoic acid gives a mixture of 8-nitro- and 5-nitro- with a trace of 1-nitro-compound (Harrison and Royle, *ibid.* 1926, 84).

## AMINONAPHTHOIC ACIDS.

The aminonaphthoic acids can generally be prepared from the corresponding hydroxynaphthoic acids by the Bucherer reaction. Exceptions are 1-hydroxy- $\beta$ -naphthoic acid and 3-hydroxy- $\beta$ -naphthoic acid which undergo decarboxylation (*idem, ibid.*). Another method is to fuse the corresponding naphthylaminesulphonic acid with potassium cyanide and then hydrolyse the nitrile (Friedländer, Heilpern, and Spielfogel, Mitt. Tech. Gewerbe Museum Wien, 1898, 316; Cassella, G.R. 92995).

2-Amino- $\alpha$ -naphthoic Acid is obtained in 90% yield by boiling naphtholisin with sulphuric acid or sodium perborate in alkaline solution (Höchst, B.P. 252820).

8-Amino- $\alpha$ -naphthoic Acid is prepared by converting  $\alpha$ -naphthylamine-8-sulphonic acid to 1-cyanonaphthalene-8-sulphonic acid (Sandmeyer reaction) and fusing this with caustic soda, the resulting naphthastyril being hydrolysed with dilute caustic soda (I.G., B.P. 276126); or by aminating 8-halogeno- $\alpha$ -naphthoic acid (Corbellini, U.S.P. 2111756), or by reduction of 8-nitro- $\alpha$ -naphthoic acid (Ekstrand, J. pr. Chem. 1888, [ii], 38, 159), or from 1:8-naphthalimide by the Hofmann reaction. It forms an internal anhydride,



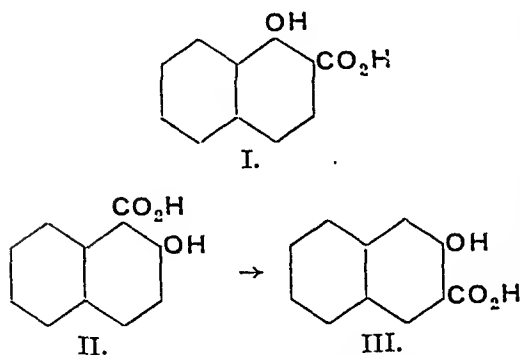
naphthastyril, of m.p. 180–181°, by dissolving in alcohol or boiling with water (*idem, ibid.*).

3-Amino- $\beta$ -naphthoic Acid is obtained from 3-hydroxy- $\beta$ -naphthoic acid by heating at about 200° with aqueous ammonia in presence of such salts as zinc chloride or ammonium chloride, yield 80% (Gessellsch., B.P. 250598) or ferrous sulphate (I.G., B.P. 282450) or iron and ammonium chloride (I.G., B.P. 309516) or by heating with the ammonia compound of zinc chloride at 240° (I.G., B.P. 284998) or with zinc oxide or carbonate and ammonium chloride at 180–200° in 70–80% yield (I.G., B.P. 330941). Yellow needles, m.p. 214°. Boiled with concentrated caustic alkalis it forms 3-hydroxy- $\beta$ -naphthoic acid.

## HYDROXYNAPHTHOIC ACIDS.

Two general methods have been used for the production of hydroxynaphthoic acids:

1. Fusion of sulphonated naphthoic acids with caustic alkali;
2. Interaction of the sodium salts of naphthols or dihydroxynaphthalenes with carbon dioxide under pressure at a suitable temperature. The acids formed from the naphthols are:



The  $\alpha$ -acid (II) from  $\beta$ -naphthol is obtained at 120–140°, and the  $\beta$ -acid (III) at 200–250°, a transformation which affords one of the rare examples in the naphthalene series of the entry of a radical into the 3-position to produce a 2:3-di-substitution derivative.

The order of stability of the three monohydroxy-acids may be inferred from the following facts:

- (i) Acid II, when heated alone or with water, loses carbon dioxide more readily than acid I; both acids by coupling furnish azo-dyes which do not contain the carboxyl group; and acid I with nitrous acid gives 2-nitroso- $\alpha$ -naphthol by elimination of the carboxyl group.
- (ii) Acid III, on the contrary, does not suffer these decompositions and loses carbon dioxide only when boiled with solutions of sodium bisulphite, ammonium bisulphite, or phenylhydrazine and bisulphite, furnishing  $\beta$ -naphthol,  $\beta$ -naphthylamine, and naphthacarbazono respectively (Bucherer, J. pr. Chem. 1905, [ii], 71, 445; Bucherer and Seyde, G.P. 208960; J. pr. Chem. 1908, [ii], 75, 403).

2-Hydroxy-3-naphthoic acid and its derivatives are used as developers in the production of azo-dyes. They are remarkable as furnishing two series of compounds, one yellow and the other colourless (Möhlau, Ber. 1895, 28, 3100).

(i) 2-Hydroxy- $\alpha$ -naphthoic Acid is obtained by acting on dry sodium  $\beta$ -naphthoxide with solid, liquid, or gaseous carbon dioxide under pressure in the cold, and subsequently heating the sodium  $\beta$ -naphthyl carbonate thus produced at 120–140° (Schmitt, G.P. 31240; Schmitt and Burkard, Ber. 1887, 20, 2701; Heyden, G.P. 38052). The acid crystallises in needles, m.p. 156–157°, but when slowly heated begins to decompose at 124–128°, and is converted quantitatively into  $\beta$ -naphthol and carbon

dioxide by prolonged boiling with water (Schmitt and Burkard, *l.c.*). With ferric chloride a deep violet-black coloration is formed. It couples with diazotised bases, but the products are azo derivatives of  $\beta$ -naphthol (Nietzki and Guter-mann, Ber. 1887, 20, 1275).

The 6-sulphonic acid is formed from 2-hydroxy- $\alpha$ -naphthoic acid by sulphonation with 20% anhydro-acid at 40° (Seidler, G.P. 53343), and its chloride by interaction with chlorosulphonic acid in the cold (Bayer, G.P. 278091). It loses carbon dioxide forming  $\beta$ -naphthol-6-sulphonic acid, either when warmed in aqueous solution at 60°, or when coupled with diazotised bases (Seidler, *l.c.*).

(ii) 3-Hydroxy- $\alpha$ -naphthoic Acid is prepared by fusion of 3-sulphonaphthalene-1-carboxylic acid or its nitrile with caustic alkali (G.P. 413836; cf. Lesser and Gad, Ber. 1925, 58 [B], 2551). It has m.p. 248–249°; acetyl derivative, m.p. 173–174°.

(iii) 4-Hydroxy- $\alpha$ -naphthoic Acid. — Its esters can be made by the interaction of  $\alpha$ -naphthol with a carbon tetrahalide in the presence of aliphatic alcohol and alkali (Gesellschaft, B.P. 181009). Heated with an arylamine, the esters give rise to arylides (Swiss. P. 99280; 100363–5; G.P. 405440). The acid has m.p. 183–184° (decomp.); acetyl derivative, m.p. 178–179° (Heller, Ber. 1912, 45, 674).

(iv) 5-Hydroxy- $\alpha$ -naphthoic Acid, from  $\alpha$ -naphthylamine-5-sulphonic acid through the derived diazo- and cyano-compounds the latter being fused with caustic alkali to replace the sulphonic group by hydroxyl, has m.p. 235–236°, acetyl derivative 202–203° (Royle and Schedler, J.C.S. 1923, 123, 1641).

(v) 6-Hydroxy- $\alpha$ -naphthoic Acid, similarly obtained from  $\alpha$ -naphthylamine-6-sulphonic acid, has m.p. 208–209°; acetyl derivative, m.p. 209–210° (*idem, ibid.*).

(vi) 7-Hydroxy- $\alpha$ -naphthoic Acid, from  $\alpha$ -naphthylamine-7-sulphonic acid, has m.p. 253–254°; acetyl derivative, m.p. 221–222° (*idem, ibid.*). It is also formed when 1:8-phthaloyl- $\beta$ -naphthol is fused with caustic soda (Riechle, Ber. 1931, 64 [B], 1603).

(vii) 8-Hydroxy- $\alpha$ -naphthoic Acid, formed, together with the anhydride or lactone (m.p. 108°), by boiling diazotised 8-amino- $\alpha$ -naphthoic acid with dilute sulphuric acid, crystallises in needles, m.p. 169° (Ekstrand, *ibid.* 1886, 19, 1138); it does not readily regenerate the lactone. It is also prepared from 1-cyano-naphthalene-8-sulphonic acid by hydrolysis with 60% sulphuric acid at 70° to the internal anhydride of 8-sulpho-1-naphthoic acid (m.p. 151–152°) followed by fusion with caustic potash at 200° (Grasselli, U.S.P. 1623678).

(viii) 1-Hydroxy- $\beta$ -naphthoic Acid is obtained from dry sodium  $\alpha$ -naphthoxide and carbon dioxide under pressure at 120–145° (Heyden, G.P. 38052), or solid, liquid, or gaseous carbon dioxide in the cold and subsequently heating the sodium  $\alpha$ -naphthyl carbonate thus produced at 120–140° (Schmitt, G.P. 31240; Schmitt and Burkard, Ber. 1887, 20, 2699). The acid crystallises in needles, m.p. 187°, is only very sparingly soluble in water (0.058 g.

in 100 c.c. at 17°), and gives with ferric chloride an intense blue coloration. The sodium salt,  $\text{NaA} + \text{H}_2\text{O}$ , scales, and the ammonium salt,  $\text{NH}_4\text{A}$ , needles, are readily soluble in hot water (Schmitt and Burkard, l.c.).

**Reactions.**—With nitrous acid it reacts to form 2-nitroso- $\alpha$ -naphthol with the elimination of carbon dioxide; nitric acid converts it into 2:4-dinitro- $\alpha$ -naphthol (Nietzki and Guitermann, *ibid.* 1887, 20, 1275) but its methyl ester undergoes nitration in the 4-position, the ester group remaining intact (Rao, Proc. Indian Acad. Sci. 1938, 7, A, 261 *et seq.*). Chlorinated in acetic acid solution, it yields 4-chloro-1-hydroxy- $\beta$ -naphthoic acid, from which carbon dioxide is readily eliminated giving 4-chloro- $\alpha$ -naphthol (Kalle, G.P.A. 45914). With diazotised nitroanilines it couples forming *para*-azo-dyes (Nietzki and Guitermann, l.c.; cf. Nietzki, G.P. 44170; 46203; B.P. 17583, 1887). The arylides have been claimed as dyestuff intermediates (I.G., B.P. 487770).

The 4-sulphonic acid is obtained from 1-hydroxy- $\beta$ -naphthoic acid by warming it with monohydrate at 60–70° until sulphonation is complete (Dahl, G.P. 51715; cf. König, Ber. 1889, 22, 787) and its chloride, m.p. 200°, by interaction with chlorosulphonic acid in the cold (Bayer, G.P. 264786; B.P. 18430, 1913). The acid,  $\text{H}_2\text{A} + 5\text{H}_2\text{O}$ , crystallising in small needles, shows blue fluorescence in alkaline solution.

Nitric acid converts it successively into 4-nitro-1-hydroxy- $\beta$ -naphthoic acid and 2:4-dinitro- $\alpha$ -naphthol (König, Ber. 1890, 23, 806). With diazotised bases it interacts, but owing to elimination of carbon dioxide, the azo-dyes formed are derivatives of  $\alpha$ -naphthol-4-sulphonic acid (König, l.c.; cf. Dahl, l.c.).

The 4:7-disulphonic acid is the main product of the sulphonation of 1-hydroxy- $\beta$ -naphthoic acid with 20% anhydro-acid at 100° (König, *ibid.* 1889, 22, 787; Seidler, G.P. 56328). The acid,  $\text{H}_2\text{A} + 4\text{H}_2\text{O}$ , needles, shows bluish-green fluorescence in alkaline solution (König, l.c.).

When boiled with 3% hydrochloric acid it yields  $\alpha$ -naphthol-4:7-disulphonic acid, but with dilute sulphuric acid at 140° it gives 7-sulpho-1-hydroxy- $\beta$ -naphthoic acid (Friedländer and Tausig, Ber. 1897, 30, 1460). Fusion with caustic alkali at 220–240° converts it into 4-sulpho-1:7-dihydroxy-2-naphthoic acid, and at a higher temperature into 1:7-dihydroxynaphthalene-4-sulphonic acid. With diazotised bases it interacts forming azo-dyes of  $\alpha$ -naphthol-4:7-disulphonic acid, owing to elimination of carbon dioxide (König, *ibid.* 1890, 23, 810). Condensed with alkylated diaminodiphenylcarbinol followed by oxidation it gives chromable wool-dyes (Bayer, B.P. 234569).

(ix) 3-Hydroxy- $\beta$ -naphthoic Acid or 2-Hydroxy-3-naphthoic Acid is the only technically important hydroxynaphthoic acid. It is obtained by the Kolbe-Schmitt reaction.  $\beta$ -Naphthol and solid caustic soda are heated together in molecular proportion. The mass fuses and, by applying vacuum, water is removed, leaving dry sodium  $\beta$ -naphthoxide. This is ground to a powder and heated at about 240° in an atmosphere of carbon dioxide at about 100 lb. pressure. The resulting car-

boxylic acid probably reacts with unchanged sodium  $\beta$ -naphthoxide, forming the disodium salt of 2:3-hydroxynaphthoic acid and free  $\beta$ -naphthol. The maximum possible yield is therefore 50% of the theory (cf. Silin and Moschtschinskaja, J. Gen. Chem. Russ. 1938, 8, 810). The reaction product is lixiviated and partly acidified to precipitate  $\beta$ -naphthol and tarry material, and from the clear filtrate the 2:3-hydroxynaphthoic acid is separated by addition of more acid.

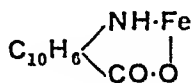
On the large scale the whole of the reaction is carried through in one vessel, which is provided with suitable means of breaking up the sodium naphthoxide by a strong stirrer; alternatively the autoclave, containing iron balls, may be rotated.

Modifications of the above method of carrying out the Kolbe-Schmitt reaction which have been suggested are (a) the use of a solvent (Calco Chem. Co., B.P. 511393), (b) the use of paraffin wax as a diluent (Cone, U.S.P. 1503984), (c) formation of  $\beta$ -naphthol-1-carboxylic acid at low temperature followed by heating as above (Schwenke, U.S.P. 1700546), (d) use of pressure (Nat. Aniline Chem. Co., U.S.P. 1725394), (e) removal of naphthol as formed (Shorey, U.S.P. 1450990).

**Identification.**—It crystallises in yellow scales, m.p. 216°, dissolves only very sparingly in hot water, and is characterised by its great stability. Its normal salts, *ethyl* ester, needles, m.p. 85°, b.p. 290–291° (Rosenberg, Ber. 1892, 25, 3634), and *hydrazide*, plates, m.p. 203–204° (Franzen and Eichler, J. pr. Chem. 1908, [ii], 78, 164) are yellow, but the *basic sodium salt*, the *O-acetyl* derivative, needles, m.p. 176–177° (Grädenwitz, Ber. 1894, 27, 2624), the *chloride*, m.p. 99°, the *amide*, m.p. 217° (Fries, *ibid.* 1925, 58 [B], 2848), the *anilide*, scales, m.p. 243–244° (Schöpf, *ibid.* 1892, 25, 2743) and arylated amides generally (Griesheim, G.P. 293897) are colourless, although the arylamides dissolve in alkalis giving yellow solutions.

**Reactions.**—On oxidation with potassium permanganate in alkaline solution it gives *o*-carboxyphenylglyoxylic acid (Schöpf, Ber. 1893, 26, 1123) and *phthalic acid* (Schmitt, l.c., p. 1114). With nitrous acid it yields 1-nitroso-2-hydroxy-3-naphthoic acid (Kostanecki, *ibid.* 1893, 26, 2898; Gulino, Ukrain. Chem. J. 1932, Tech. 197). The nitroso compound can be treated with iron salts to give pigments (Badische, G.P. 350322). Treated with sodium bisulphite it gives a compound which, on acidification, loses carbon dioxide and gives 1-nitroso- $\beta$ -naphthol-4-sulphonic acid (Lanz and Mingasson, Bull. Soc. chim. 1931, [iv], 49, 1172). Monohydrate at 60° gives a mixture of the 6- and 8-sulphonic acids, but chlorosulphonic acid in the cold the 1-sulphonyl chloride, m.p. 219° (Bayer, G.P. 264786; B.P. 18430, 1913). Bromination gives 1:6-dibromo-2-hydroxy-3-naphthoic acid (I.G., B.P. 378676) which can be reduced to the 6-bromo-compound with mild alkaline reducing agents (I.G., B.P. 381947). The latter can be converted to the 6-amino-compound (I.G., B.P. 462699). With diazotised bases it couples, forming azo-dyes, without elimination of the carboxyl group (Kostanecki, l.c.; cf. Aktienges.,

G.P. 77286; B.P. 15789, 1892; Sircar and Watson, J.S.C.I. 1913, 32, 642). Oxidation with ferric chloride gives rise to 2:2'-*dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid*, m.p. 331-333° (decomp.), resolvable into optical isomers (Stanley and Adams, Rec. trav. chim. 1929, 48, 1035). Condensation with aliphatic diamines in the presence of sodium bisulphite produces  $\omega$ -aminoalkylaminoalkyl-compounds, e.g.,  $\beta$ -naphthyl- $\omega$ -aminoethylamine (Bayer, B.P. 249717). Heated with ferrous sulphate and ammonia under pressure at 200-210°, an iron compound,



is formed which is decomposed by hydrochloric acid to give 2-amino-3-naphthoic acid (I.G., B.P. 282450; see also Möhlau, Ber. 1895, 28, 3096).

**Arylamides.**—The arylamides or "arylides" of 2-hydroxy-3-naphthoic acid have assumed considerable importance as components of the Azoic dyes or Ice colours. The anilide was first used as source of azo-dyes by being coupled with diazotised primuline (Badische, G.P. 221481), but later, under the name "Naphthol AS," was introduced as a developer for brilliant shades on the fibre, replacing  $\beta$ -naphthol. For further information on the technical application of the arylamides, see DYE-STUFFS, Azo, Vol. IV, 227.

The arylamides are prepared by heating 2:3-hydroxynaphthoic acid and the appropriate amino in molecular proportion in a suitable solvent, e.g., toluene, with a condensing agent such as phosphorus trichloride or thionyl chloride. The charge is then made alkaline with soda ash and the solvent distilled off with steam. The insoluble arylide is filtered, washed with acid to remove any remaining amine and dried. Tertiary bases can be used as the solvent (British Synthetics, Ltd. and Higgins, B.P. 262958 and 268877).

The anilide reacts with nitrous acid, forming [ $\beta$ -naphthaquinoneoxime-3-carboxyanilide which as sodium salt can be converted by sodium bisulphite into a bisulphite compound, which is claimed to dye cotton better than the corresponding  $\beta$ -naphthol derivative. The quinone-oxime can be reduced to 1-amino-2-naphthol-3-carboxyanilide, m.p. 180° (Battagay, Langjahr, and Rettig, Chim. et Ind. 1924, 11, 453; Battagay and Riesz, Bull. Soc. chim. 1932, [iv], 51, 902). The arylides condense with formaldehyde to give 1:1'-dinaphthylmethane compounds; hence the stabilisation of "Naphthol AS" baths by formaldehyde is attributed to the formation of substances of this type (Brass and Sommer, Ber. 1928, 61 [B], 993). As formaldehyde may itself produce deleterious effects on the dyes, an alternative proposed is to replace the hydrogen atom in the —CONHR group of the arylide by an aromatic quaternary ammonium radical, the arylide, for example, being heated with pyridiniummethyl iodide (British Synthetics, Ltd., B.P. 230920).

Arylamides sulphonated with monohydrate at

90° furnish sulphonic acids of value as dyestuff intermediates (Höchst, B.P. 183428).

Arylamides sulphonated in the arylamino-part of the molecule can be obtained, e.g., by using *o*-, *m*-, and *p*-anilinesulphonic acids in the general method of condensation, pyridine being used as solvent (Voroschev and Genkin, J. Gen. Chem. Russ. 1938, 8, 357).

Nuclear substituted methoxy derivatives can be prepared by Kolbe's reaction from the corresponding methoxy- $\beta$ -naphthols (I.G., B.P. 366140), and 5-, 6-, and 7-arylamino derivatives by heating the alkali salt of the corresponding arylamino- $\beta$ -naphthol with carbon dioxide under pressure (I.G., B.P. 382449).

The 6-sulphonic acid and the 8-sulphonic acid, obtained by sulphonating 2-hydroxy-3-naphthoic acid with monohydrate at 60° or above, are separated as calcium salts, that of the 6-sulphonic acid being the more soluble in hot water (Gesellsch., G.P. 69357; Schmid, Ber. 1893, 26, 1118; Hirsch, *ibid.* 1177), or as acid sodium salts, that of the 6-sulphonic acid being the less soluble (Bucherer, cf. J.S.C.I. 1903, 22, 945). The 6-acid couples readily, but the 8-acid only slowly with diazo-compounds.

The 6:8-disulphonic acid is the chief product of the sulphonation of 2-hydroxy-3-naphthoic acid with 24% anhydro-acid at 125-150° (Gesellsch., G.P. 67000; B.P. 14161, 1892). Fusion with caustic soda at 210-240° converts it into 3-sulpho-1:7-dihydroxy-6-naphthoic acid (Gesellsch., *l.c.*; cf. G.P. 71202; Schmid, *l.c.*). With ammonium solution at 240-280°, it gives 6-sulpho-2-amino-8-hydroxy-3-naphthoic acid (Gesellsch., G.P. 69740).

(x) 4-Hydroxy- $\beta$ -naphthoic Acid was first claimed to be prepared from 4-amino-2-naphthonitrile by Butler and Royle (J.C.S. 1923, 123, 1649), but there appears to be an error in their results since the melting-point of their product was appreciably lower than that obtained by Cason (J. Amer. Chem. Soc. 1911, 63, 828) by the same method. It has also been prepared from 4-chloro-3-amino- $\beta$ -naphthoic acid through the diazo-oxide (Luce, G.P. 523358). Haworth, Jones, and Way (J.C.S. 1943, 10) have synthesised it from benzylsuccinic acid by conversion with aluminium chloride to 4-keto-1:2:3:4-tetrahydronaphthoic acid which was brominated to 3-bromo-4-keto-1:2:3:4-tetrahydronaphthoic acid from which HBr was eliminated by heating with diethylaniline to give 4-hydroxy- $\beta$ -naphthoic acid.

The acid has m.p. 225-226°; acetyl-compound, m.p. 211-212° (Cason, *l.c.*).

(xi) 5-Hydroxy- $\beta$ -naphthoic Acid, obtained by fusing the corresponding sulphonaphthoic acid with caustic potash, has m.p. 211°; acetyl-compound, m.p. 214-215° (Butler and Royle, *l.c.*).

(xii) 6-Hydroxy- $\beta$ -naphthoic Acid, by the same method, has m.p. 240-241°; acetyl, m.p. 221-223° (*l.c.*). It is obtained with the 3:2-isomer by the Kolbe-Schmitt method using potassium  $\beta$ -naphthoxide instead of sodium  $\beta$ -naphthoxide (Grasselli, U.S.P. 1593816). Its arylides can be used for azoic colours (Bayer, G.P. 294798). On sulphonation with concentrated sulphuric acid at 50-80° it gives a

separable mixture of the 4- and 7-isomers and with oleum the 4:7-disulphonic acid (I.G., B.P. 291965).

(xiii) 7-Hydroxy- $\beta$ -naphthoic Acid from 7-amino-2-naphthonitrile has m.p. 269–270°; *acetyl*-compound, m.p. 209–210° (Butler and Royle, l.c.).

(xiv) 8-Hydroxy- $\beta$ -naphthoic Acid, by a similar method to the 5-isomer, has m.p. 228–229°; *acetyl*-compound, m.p. 176–177° (*idem*, *ibid.*).

#### DIHYDROXYNAPHTHOIC ACIDS.

Of the dihydroxynaphthalenecarboxylic acids, six, namely those containing the radicals OH:OH:CO<sub>2</sub>H in the 1:2:3-, 1:4:2-, 1:6:(?), 1:7:(?), 1:8:2-, and 2:7:(3)-positions, have been obtained by interaction of the heated sodium salts of the respective dihydroxynaphthalenes with carbon dioxide under pressure (cf. Möhlau, Ber. 1893, 26, 3067; 1895, 28, 3093; Schmid, *ibid.* 1893, 26, 1117; Russig, J. pr. Chem. 1900, [ii], 62, 33; Hemmelmayer, Monatsh. 1917, 38, 84; Heyden, G.P. 55414), and two containing these radicals respectively in the 3:5:2- and 3:7:2-positions, by fusion of the corresponding sulpho-3-hydroxy- $\beta$ -naphthoic acids with caustic alkali (cf. Schmidt l.c.; Gesellsch., G.P. 69357). 1:4-Dihydroxynaphthalene-2-carboxylic acid has been obtained by synthesis from ethyl phthalate and ethyl succinate (Homes and Wallingford, J. Amer. Chem. Soc. 1942, 64, 798).

(i) 2:7-Dihydroxy- $\alpha$ -naphthoic Acid, m.p. 275°, is prepared from 2:7-dihydroxynaphthalene (Passerini, Gazzetta, 1924, 54, 633) by reaction with phenylcarbylamine, an intermediate “dianil” compound being formed.

(ii) 1:7-Dihydroxy- $\beta$ -naphthoic Acid (m.p. 222°) is produced by hydrolysis of 1:7-dihydroxy-4-sulpho- $\beta$ -naphthoic acid. The 4-sulphonic acid is produced by fusing 4:7-disulpho-1-hydroxy- $\beta$ -naphthoic acid with 80% caustic soda solution at 190° (Bindschedler, G.P. 84653; B.P. 4630, 1894), or with caustic soda at 220–240° (Friedländer and Zinberg, Ber. 1896, 29, 38). It couples with diazotised bases (Bindschedler, l.c.) and is converted into 1:7-dihydroxynaphthalene-4-sulphonic acid when heated with 30% caustic soda at 140–160° (Bindschedler, G.P. 83965), but into 1:7-dihydroxy- $\beta$ -naphthoic acid when either boiled with 20% hydrochloric acid (Bayer, G.P. 89539), or heated at 140° with 50% sulphuric acid (Friedländer and Zinberg, l.c.).

(iii) 3:5-Dihydroxynaphthalene- $\beta$ -naphthoic Acid.—The 7-sulphonic acid (*nigrotic acid*; cf. Bucherer, J. pr. Chem. 1907, [ii], 75, 287), obtained by fusing 6:8-disulpho-2-hydroxy-3-naphthoic acid with caustic soda at 210–240° (Gesellsch., G.P. 67000; B.P. 14161, 1892; Schmid, Ber. 1893, 26, 1119) shows yellowish-green fluorescence in alkaline solution. It couples with diazotised bases forming black or grey azo-dyes (Gesellsch., G.P. 71202; 75258; 80912; 84546; B.P. 14253, 1892; 4460, 1894).

(iv) 3:7-Dihydroxy- $\beta$ -naphthoic Acid, derived from 2-hydroxy-3-naphthoic acid by sulphonation and fusion with caustic soda (Gesellsch., G.P. 69357) has been used for chrome azo-dyes (I.G., B.P. 270308). With ammonia it

gives 7-amino-3-hydroxy- $\beta$ -naphthoic acid, m.p. 295° (I.G., B.P. 326971; 334700).

(v) 4:6-Dihydroxy- $\beta$ -naphthoic Acid is obtained by sulphonating 6-hydroxy- $\beta$ -naphthoic acid and fusing the product with alkali. It couples with diazotised bases to form dyes for wool (I.G., B.P. 302770).

#### NAPHTHALENEDICARBOXYLIC ACIDS.

The naphthalenedicarboxylic acids, except the 1:8-isomer, are of little technical importance. The dinitriles of the 1:2- and 2:3-acids give green phthalocyanine dyes (Bradbrook and Linstead, J.C.S. 1936, 1739).

The complete series of dicarboxylic acids is known. They can be made by converting an aminosulphonic acid into the corresponding cyanosulphonic acid and fusing the alkali salt with alkali ferrocyanide or cyanide (Bradbrook and Linstead, l.c.). The melting-points of methyl esters and dinitriles quoted below are from Bradbrook and Linstead's paper.

(i) Naphthalene-1:2-dicarboxylic Acid, m.p. 175°, can be obtained from sodium  $\alpha$ -chloronaphthalene-2-sulphonate, through the dinitrile. Sublimed in a vacuum at 180–200°, the *anhydride*, m.p. 160°, is formed (Waldmann and Weiss, J. pr. Chem. 1930, [ii], 127, 197; cf. Cook, J.C.S. 1932, 462). The methyl ester has m.p. 85°, *dinitrile*, m.p. 190°.

(ii) Naphthalene-1:3-dicarboxylic Acid, m.p. 267–268° is obtained from  $\alpha$ -naphthylamine-3-sulphonic acid (Bradbrook and Linstead, l.c.). The *dinitrile* has m.p. 190°.

(iii) Naphthalene-1:4-dicarboxylic Acid is made by the oxidation of 1-methyl-4-naphthoic acid with potassium permanganate (Mayer and Sieglitz, Ber. 1922, 55 [B], 1841), or by conversion of naphthalene-1:4-disulphonic acid into the dinitrile, followed by hydrolysis (Scholl and Neumann, *ibid.*, p. 118). It melts at 309° (cf. 288°, given by Mayer and Sieglitz, l.c.) and the *chloride* at 80° (Scholl and Neumann, l.c.). The methyl ester has m.p. 67°, *dinitrile*, 208°.

(iv) Naphthalene-1:5-dicarboxylic Acid, m.p. 300°, gives a *chloride*, m.p. 155–156° (I.G., B.P. 336800), methyl ester, m.p. 119°; *dinitrile*, m.p. 263°.

(v) Naphthalene-1:6-dicarboxylic Acid is obtained by oxidation of 1:6-dimethylnaphthalene, a product of the dehydrogenation of iron. It melts with decomposition at about 305° (Ruzicka and Rudolph, Helv. Chim. Acta, 1927, 10, 915). Methyl ester, m.p. 98°; *dinitrile*, m.p. 211°.

(vi) Naphthalene-1:7-dicarboxylic Acid is produced when *eudalene* (1-methyl-7-isopropylnaphthalene) is oxidised by nitric acid. It is fairly soluble in alcohol or ether and melts at about 265° (Ruzicka and Stoll, *ibid.* 1922, 5, 923). Methyl ester, m.p. 90°; *dinitrile*, m.p. 167°.

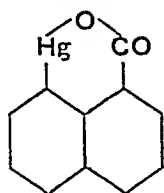
(vii) Naphthalene-1:8-dicarboxylic Acid (*naphthalic acid*) is obtained by the oxidation of acenaphthene with chromic acid (Behr and Van Dorp, Annalen, 1874, 172, 266; Anselm, Ber. 1892, 25, 652) or in 95% yield by oxidising acenaphthenequinone in caustic soda suspension

by excess of hydrogen peroxide (Whiston, J.S.C.I. 1924, 43, 370r).

**Identification.**—It crystallises from alcohol in needles, m.p. 270–271° (Leuck, Perkins, and Whitmore, J. Amer. Chem. Soc. 1929, 51, 1831). The *dichloride* has m.p. 84–86° (Mason, J.C.S. 1924, 125, 2116), the *ethyl ester*, m.p. 59–60° (Wislicenus and Penndorf, Ber. 1912, 45, 410), *methyl ester*, m.p. 104°; *dinitrile*, m.p. 232°. It readily forms an *anhydride*, m.p. 274°, and *imide*, m.p. 300° (Terisse, Annalen, 1885, 227, 135).

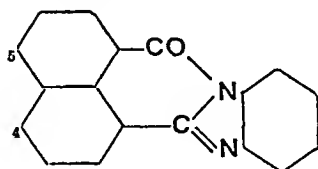
**Reactions and Uses.**—3-Aminonaphthalic acid (Gesellsch., B.P. 246394), 4-aminonaphthalic acid (I.G., B.P. 352139), and 4-aminonaphthalimide (I.G., B.P. 304739; 309552) have been patented as dyestuff intermediates.

Naphthalic acid reacts with mercuric acetate to give *anhydro-8-hydroxymercuri- $\alpha$ -naphthoic acid* (I), convertible by acid hydrolysis to  $\alpha$ -



I.

naphthoic acid, and by bromine to 8-bromo- $\alpha$ -naphthoic acid, an intermediate for the production of anthanthrone. 3- and 4-Nitronaphthalic acids by mercuration give mixtures of two isomeric nitro derivatives of (I) in each case (Leuck, Perkins, and Whitmore, *loc. cit.*; Davies, Heilbron, and Irving, J.C.S. 1932, 2715). Naphthalic anhydride with *o*-phenylenediamine and its substitution derivatives forms *naphthylenebenziminazoles* of type II (I.G., B.P. 316143). By oxidation in the 4:5-positions these



II.

compounds, and the N-substituted naphthalimides, form perylene derivatives which are an important class of vat dye (*v. ANTHRAQUINONE DYE STUFFS*, Vol. I, p. 427).

(viii) Naphthalene-2:3-dicarboxylic Acid is prepared from 3-amino-2-naphthoic acid through the 3-cyano derivative. It melts at about 236° (Waldmann, J. pr. Chem. 1930, [ii], 128, 150; I.G., B.P. 332122), and when sublimed is converted into the *anhydride*, m.p. 246° (Waldmann and Mathiowetz, Ber. 1931, 64 [B], 1716). The *methyl ester* has m.p. 47°; *nitrile*, m.p. 251°.

(ix) Naphthalene-2:6-dicarboxylic Acid is made from  $\beta$ -naphthylamine-6-sulphonic acid (Bröner acid); m.p. above 300° (Bradbrook and Linstead, *loc. cit.*). The *methyl ester* has m.p. 186°; *nitrile*, m.p. 293°.

(x) Naphthalene-2:7-dicarboxylic Acid.—2:7-Dicyanonaphthalene, m.p. 261°, prepared from dry sodium naphthalene-2:7-disulphonate, is converted into the dicarboxylic acid on

hydrolysis. The *methyl ester* melts at 191°, the *ethyl ester* at 238°. On nitration, the acid gives rise to di- and tri-nitro-compounds, and on oxidation with permanganate furnishes trimellitic acid (Pargotti, A, 1926, 951). Bradbrook and Linstead give m.p. 135° for the *methyl ester*; 267° for the *dinitrile*.

#### HYDROXYNAPHTHALENEDICARBOXYLIC ACIDS.

1-Naphthol-2:4-dicarboxylic Acid.—Its esters are made from 1-hydroxy-2-naphthoic acid by interaction with a carbon tetrahalide in presence of an aliphatic alcohol and alkali. It decomposes at about 286° (Gesellsch., B.P. 181009; 195513; G.P. 373736).

2-Naphthol-3:6-dicarboxylic Acid.—Its *diaryldyes* are used for making water-insoluble azo-dyes (Griesheim, F.P. 601687; B. 1927, 212).

**Hydroxynaphthalic Acids.**—Dzięwoński and his co-workers have investigated several of the naphthol-1:8-dicarboxylic acids in the course of work on acenaphthene. By sulphonation of acenaphthene, followed by oxidation and fusion with caustic potash at 250°, 2-hydroxynaphthalic anhydride, m.p. 242°, was made (Bull. Acad. Polonaise, 1926, A, 209). 4-Chloronaphthalic anhydride and 4-bromonaphthalaminoimide, on alkali fusion, give 3-hydroxynaphthalic anhydride, m.p. 280° (*idem, ibid.* 1927, A, 65; 1928, A, 507). The 2-, 3-, and 4-sulphonaphthalic acids have been described (*idem, ibid.* 1928, A, 405), and the mode of coupling of the three corresponding hydroxy-compounds investigated. 3-Hydroxynaphthalic acid couples normally in the 4-position, but 2- and 4-hydroxynaphthalic acids exchange the 1-carboxyl group for the azo-group (*idem, Ber.* 1924, 57 [B], 1540).

3-Hydroxynaphthalic acid is stated to give mordant dyes (Gesellsch., B.P. 226797; Karpuschin and Ratnikova, Ukrain. Chem. J. 1937, 122).

#### DIHYDROXYNAPHTHALENEDICARBOXYLIC ACIDS.

3:4-Dihydroxynaphthalic Acid, m.p. 330°, is obtained from naphthalic acid by disulphonation and fusion of the resulting 3:4-disulphonaphthalic acid with caustic alkali (Dzięwoński and others, Bull. Acad. Polonaise, 1928, A, 507). Its *anhydride*, m.p. 324°, forms coloured lakes with iron, chromium, and aluminium salts (*ibid.* 1931, A, 531).

2:7-Dihydroxynaphthalene-3:6-dicarboxylic Acid is obtained when the alkali salt of 2:7-dihydroxynaphthalene or its 3-carboxylic acid is heated with carbon dioxide under pressure. Its *pyridinium salt* is sparingly soluble (I.G., B.P. 395365).

1:5-Dihydroxynaphthalene-2:6-dicarboxylic Acid is probably the constitution of the product formed by heating 1:5-dihydroxynaphthalene with potassium bicarbonate at 230°. It decomposes at 290°, is nearly insoluble in water and its alkali salts show a blue fluorescence in aqueous solution (Hömmelmayer, Monatsh. 1917, 38, 84; 1922, 43, 61; G.P. 296035; 296501).



## NAPHTHALENEPOLYCARBOXYLIC ACIDS.

A *naphthalenetetracarboxylic acid* is obtained on oxidation of the terpene amyrin. It is characterised by its *methyl ester*, m.p. 153–154°, and *ethyl ester*, m.p. 80–81° (Ruzicka, Huyser, Pfeiffer, and Seidel, *Annalen*, 1929, 471, 21).

*Naphthalene-1:4:5:8-tetracarboxylic Acid* results from oxidation of the condensation product of acenaphthene with malonyl chloride (Höchst, B.P. 240859) and nuclear substitution derivatives arise from oxidation of the corresponding acenaphthalic acids (I.G., B.P. 400069). A similar preparation can be carried out using succinic anhydride instead of malonyl chloride (I.G., B.P. 273321; 274103) or pyrenequinone can be oxidised with alkali hypochlorite (I.G., B.P. 449192) or di, tri-, and tetra-halogenopyrenes can be heated with concentrated sulphuric acid and the products oxidised (I.G., B.P. 421813). Its mono- and di-anhydrides can be used as sources of dyestuffs (I.G., B.P. 364544). By condensation with aromatic *o*-diamines the dianhydride forms *naphthoylenebenziminazoles* some of which are important vat dyes (*v.* ANTHRAQUINONE DYESTUFFS, Vol. I, p. 427).

## QUINONES.

Of the three possible homonuclear naphthaquinones only the 1:2- and 1:4- are known. Derivatives of 2:3-naphthaquinone are said to have been prepared, but Fieser (*J. Amer. Chem. Soc.* 1930, 52, 5219) from a comparison of the oxidation-reduction potentials of 2:3- and 2:6-dihydroxynaphthalenes concludes that the 2:3-isomer cannot form a quinone (*cf.* Fries and Schimmelschmidt, *Ber.* 1932, 65 [B], 1502). Of the three possible heteronuclear naphthaquinones only the 2:6 has been isolated. The so-called 1:8-naphthaquinone of Meldola and Hughes (*J.C.S.* 1890, 57, 632) was subsequently found to be a dinaphthaquinone (Liebermann and Schlossberg, *Ber.* 1899, 32, 546; *cf.* Meldola, *ibid.*, p. 868).

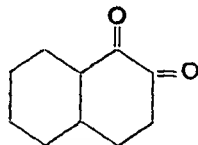
Naphthaquinone derivatives occur in nature, to some extent, as plant colouring matters (*see* Macbeth, Price, and Winsor, *J.C.S.* 1935, 325; Price and Robinson, *Nature*, 1938, 147). Important natural derivatives are the anti-hæmorrhagic vitamins (*K* group) (*see* K-VITAMIN, Vol. VII, 87a). These are discussed under alkylnaphthalenes (*see also* H. R. Rosenberg, "Chemistry and Physiology of the Vitamins," 1942, Interscience Publishers, Inc., New York).

The naphthaquinones are coloured substances. Some of the azo-dyes obtained by coupling diazo-compounds with  $\alpha$ - or  $\beta$ -naphthol are identical with the phenylhydrazones of naphthaquinones. The naphthaquinones themselves are only important for dyestuffs production when they or their derivatives can form coloured chelate compounds with metallic oxides; such metal complexes can be formed, for example, by  $[\beta]$ -naphthaquinone-1-oxime, which is tautomeric with 1-nitroso- $\beta$ -naphthol (*cf.* Kostanecki, *Ber.* 1887, 20, 3147). The iron "lake" of this compound is a technically important pigment.

The constitution of such "lakes" has been

discussed in papers by Tschugaëff (*J. pr. Chem.* 1907, [ii], 11, 76, 88); Werner (*Ber.* 1908, 41, 1062, 2383); Liebermann (*ibid.*, p. 1436); Morgan (*J. Soc. Dyers and Col.* 1921, 37, 43). The constitution of the most important, Pigment Green B, the iron complex of 1-nitroso- $\beta$ -naphthol, is still not clear. Morgan and Moss (*J.C.S.* 1922, 121, 2857) remark that the iron lakes of quinoneoxime dyes are usually cited as ferrous compounds but that there is no evidence for this, and that green quinoneoxime-iron lakes can be produced either from ferric or ferrous salts, but in the latter instance lake formation is accompanied by oxidation. It is difficult to visualise that this can be the case with Pigment Green B which is usually prepared by interaction of a ferrous salt with the bisulphite compound of nitroso- $\beta$ -naphthol. Robinson (*J. Soc. Dyers and Col.* 1921, 37, 229) differentiates between two types of metal compounds of nitroso- $\beta$ -naphthol; a basic type (green) in which 1 atom of ferric iron combines with 2 mol. of nitroso- $\beta$ -naphthol and a normal ferrous compound (green) in which 1 atom of ferrous iron combines with 2 mol. of nitroso- $\beta$ -naphthol. The method of making Pigment Green B as described in G.P. 356973 (Badische), in which a ferrous salt reacts with the bisulphite compound of nitroso- $\beta$ -naphthol, specifically states that the usage of ferrous salt should be only 1 atom of iron to 3 mol. of nitroso- $\beta$ -naphthol. There is insufficient published evidence to clarify the constitution completely but analysis of Pigment Green B shows it to contain approximately not only iron (1 atom) but sodium (1 atom) to 3 mol. of nitroso- $\beta$ -naphthol (private communication).

(i)  $[\beta]$ -Naphthaquinone (1:2-Naphthaquinone),



is obtained by oxidation of 1-amino- $\beta$ -naphthol by chromic acid or ferric chloride (*see* preparation) or by oxidation of 2-amino- $\alpha$ -naphthol by nitrous acid (Grandmougin and Michel, *Ber.* 1892, 25, 3430).

*Preparation.*—This is very fully described by Fieser in *Organic Syntheses*, Vol. XVII, p. 68. In brief, 80 g. 1-amino- $\beta$ -naphthol hydrochloride is dissolved in 3 litres of water containing 5 c.c. of concentrated hydrochloric acid. A solution of 240 g.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 500 c.c. water and 90 c.c. of concentrated hydrochloric acid is then added all at once with good agitation. The  $[\beta]$ -naphthaquinone separates immediately in a voluminous microcrystalline form which is filtered and well washed and dried on filter paper at room temperature in absence of acid fumes. The yield is 60–61 g. (93–94% theory). The product for all practical purposes may be considered pure.

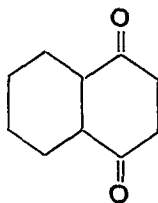
*Identification.*—As prepared above it consists of microcrystalline, pure golden-yellow needles, m.p. 145–147° (decomp.). If crystallised from alcohol it may be obtained as orange-red needles but the decomposition point is lowered by 10–20°



(Fieser, *l.c.*; cf. Liebermann and Jacobson, *Annalen*, 1882, 211, 49).  $\beta$ -Naphthaquinone differs from the  $\alpha$ -isomer in being odourless and non-volatile in steam. It dissolves in dilute alkalis giving yellow solutions which rapidly oxidise with air. The crystal structure has been determined by X-ray examination by Caspari (Proc. Roy. Soc. 1932, A, 136, 82).

**Reactions.**—By sulphurous or hydriodic acid it is reduced to 1:2-dihydroxynaphthalene but with stannous chloride to  $\beta$ -dinaphthaquinol (Stenhouse and Groves, J.C.S. 1878, 33, 415). Oxidation with ferric chloride gives mainly 3-hydroxy-2:2'-dinaphthyl-1:4:3':4'-diquinone (Hooker and Fieser, J. Amer. Chem. Soc. 1936, 58 [B], 1216) which is the so-called di- $\beta$ -naphthaquinone oxide of Wichelhaus (Ber. 1897, 30, 2199). With nitric acid it gives first 3-nitro- $\beta$ -naphthaquinone (Zaertling, *ibid.* 1890, 23, 175) and finally phthalic acid (Stenhouse and Groves, *l.c.*), but with permanganate or dichromate only phthalic acid is obtained (Boswell, J. Physical Chem. 1907, 11, 119). Oxidation with peracetic acid gives  $\alpha$ -carboxyalloxiannamic acid (Böseken and Sloof, Rec. trav. chim. 1930, 49, 91). Chlorinated in acetic acid it gives 3-chloro- and 3:4-dichloro derivatives (Zineke, Ber. 1886, 19, 2497). With phenylhydrazine it gives the 2-hydrazoic, m.p. 138° (red needles), isomeric with benzeneazo- $\beta$ -naphthol (Bamberger *ibid.* 1897, 30, 514) and with hydroxylamine the monoxime, identical with 2-nitroso- $\alpha$ -naphthol (Goldschmidt, *ibid.* 1884, 17, 215). It reacts with hydrazoic acid to give 4-amino- $\beta$ -naphthaquinone (Fieser and Hartwell, J. Amer. Chem. Soc. 1935, 57, 1482). With aniline it yields 2-hydroxy- $\alpha$ -naphthaquinone-4-acyl convertible to 2-anilino- $\alpha$ -naphthaquinone (Liebermann and Jacobson, *l.c.*; Zineke, Ber. 1881, 14, 1494). With 1:2:4-triaminobenzene it gives 3-amino-naphthophenazine (Kochmann and Mermod, Helv. Chim. Acta, 1927, 10, 62). With acetic anhydride and sulphuric acid or zinc chloride or phosphoric acid the triacetate of 1:2:4-trihydroxynaphthalene is formed. With strong sodium bisulphite solution 1:2-dihydroxynaphthalene-4-sulphonic acid is obtained and with thiosulphate and acetic acid 1:2-dihydroxynaphthalene-4-thiosulphonic acid (Bayer, G.P. 71314; B.P. 825, 1893). With sulphuric acid it gives a black dyestuff for mordanted wool (Heyden, G.P. 113336; B.P. 3265, 1900); it may also be converted into vat dyestuffs (Kallo, G.P. 286151).

(ii)  $\alpha$ -Naphthaquinone (1:4-Naphthaquinone),



is obtained by oxidation of naphthalene with chromic acid in acetic acid (Groves, J.C.S. 1873, 26, 209) or by oxidation of 1:4-diaminonaphthalene with nitrous acid (Grandmougin and Michel, Ber. 1892, 25, 977) or by oxidation of  $\alpha$ -naphthyl-

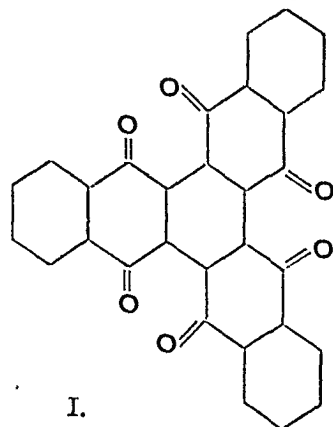
amine or its 4-sulphonic acid with chromic acid (Monnet, Reverdin, and Noeltling, *ibid.* 1879, 12, 2306).

**Preparation.**—A convenient method of preparation from 1:4-aminonaphthol hydrochloride is fully described by Fieser in Organic Syntheses, Vol. XVII, p. 69. In brief, 70 g. 4-amino- $\alpha$ -naphthol hydrochloride is dissolved in 2,100 c.c. water at 30°, 100 c.c. of concentrated sulphuric acid added, and the mixture heated to boiling to dissolve the precipitated sulphate. The hot solution is filtered, the filtrate delivering directly into a cold filtered solution of 70 g. potassium dichromate in 1 litre of water. The  $\alpha$ -naphthaquinone separates as fine yellow needles which are filtered, washed, and dried at 30–40°. The crude product melts at 124–125° and can be recrystallised from ether. The yield is 44–46 g. (78–81% theory) and the melting-point of the purified product 124–125°. It may also be purified by sublimation in steam under reduced pressure (*idem*, *ibid.*, Vol. V, p. 79).

**Identification.**—It crystallises in yellow needles, m.p. 125°, begins to sublime below 100°, and is readily volatile in steam. It has the same characteristic odour as *p*-benzoquinone, is readily soluble in most organic solvents but only sparingly soluble in water or light petroleum. W. A. Caspari (Proc. Royal Soc. 1932, A, 136, 82) has made an X-ray examination of its crystal structure.

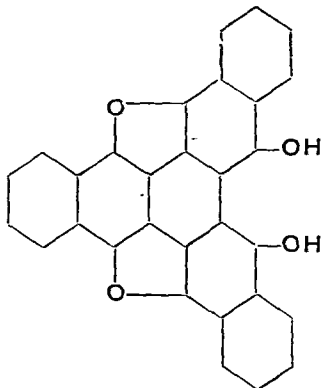
**Reactions.**—It is not reduced in the cold by sulphurous acid, but with tin and hydrochloric acid, or hydriodic acid and phosphorus is reduced to 1:4-dihydroxynaphthalene. Partial reduction leads to naphthaquinhydrone. In caustic soda solution atmospheric oxidation gives 2-hydroxy- $\alpha$ -naphthaquinone, but with nitric acid or permanganate, phthalic acid is formed (Liebermann and Dittler, *Annalen*, 1876, 183, 243; Japp and Miller, J.C.S. 1881, 39, 220). In acetic acid solution chlorine gives the dichloride, m.p. 176°, and bromine the dibromide, m.p. 92° (Zineke and Schmidt, Ber. 1894, 27, 2757).

$\alpha$ -Naphthaquinone undergoes condensation reactions in which 3 mol. participate to form derivatives of trinaphthobenzene. When heated under pressure with water at 120–130° (Badische, G.P. 350738) it is converted into  $\alpha$ -naphthaquinol and a complex yellow substance, reducible by hydrosulphite, which has been identified as triphthaloylbenzene (I) (Pumnerer, Lüttringhaus



I.

*et al.*, Ber. 1938, 71 [B], 2569). By condensation in sulphuric and acetic acids [ $\alpha$ ]-naphthaquinone gives a mixture of the bis-anhydro-compound of the corresponding naphthaquinol (II) (diacetate, m.p. 340–343°), and the trianhydro-compound, *trinaphthobenzene-trioxide*,



II.

subliming at 300–330°/high vac. (Erdtmann, Proc. Roy. Soc. 1933, A, 143, 240). The last compound is also formed by the action of aluminium chloride on [ $\alpha$ ]-naphthaquinone in nitrobenzene at 50°, in high yield. It is insoluble in organic solvents, and gives a green solution in 20% oleum, turning violet on the water-bath (Marschalk, Bull. Soc. chim. 1938, [v], 5, 304).

With phenylhydrazine, [ $\alpha$ ]-naphthaquinone yields the hydrazone, identical with *benzeneazo- $\alpha$ -naphthol* (Zincke and Bindewald, Ber. 1884, 17, 3026); the latter boiled with 10% acetic acid gives the isomeric 2-anilino- $\alpha$ -naphthaquinone (I.G., G.P. 470760) which is also formed by direct action of aniline on [ $\alpha$ ]-naphthaquinone in alcoholic solution. With hydroxylamine the *monoxime* is obtained identical with 4-nitroso- $\alpha$ -naphthol (Goldschmidt and Schmid, Ber. 1884, 17, 2064). It reacts with hydrazoic acid to give 2-amino- $\alpha$ -naphthaquinone (Fieser and Hartwell, J. Amer. Chem. Soc. 1935, 57, 1482). With pyridine hydrobromide it reacts to form 1:4-dihydroxynaphthalene-3-pyridinium bromide (Barnett, Cook, and Driscoll, J.C.S. 1923, 123, 503). Unsaturated hydrocarbons such as butadiene or isoprene react with [ $\alpha$ ]-naphthaquinone or its derivatives to give anthraquinone derivatives (Diels and Alder, Annalen, 1928, 460, 98; I.G., B.P. 320375; Fieser and Dunn, J. Amer. Chem. Soc. 1937, 59, 1016). Its use in preparation of vat dyestuffs is described in G.P. 267414 and 267415 (Cassella), G.P. 286151 (Kalle), G.P. 398878 (Cassella).

**Chloro Derivatives.**—Several of the chloro derivatives of [ $\alpha$ ]-naphthaquinone have been prepared by oxidation of chloro derivatives of naphthalene or naphthols. Thus, 2-chloro- $\alpha$ -naphthaquinone is obtained by chromic acid oxidation of 1:3-dichloronaphthalene (Cleve, Ber. 1890, 23, 955) or of 2:4-dichloro- $\alpha$ -naphthol (Zincke, *ibid.* 1888, 21, 1036); 2:6-dichloro- $\alpha$ -naphthaquinone (m.p. 148–149°) by chromic acid oxidation of 2:6-dichloronaphthalene (Claus

and Müller, *ibid.* 1885, 18, 3075); 5:6-dichloro- $\alpha$ -naphthaquinone (m.p. 181°), by chromic acid oxidation of 1:2-dichloronaphthalene (Hellström, *ibid.* 1888, 21, 3269); 5:8-dichloro- $\alpha$ -naphthaquinone by oxidation of 1:4-dichloronaphthalene (Guareschi, *ibid.* 1886, 19, 1155). 6-Chloro- $\alpha$ -naphthaquinone has been prepared from  $\beta$ -chlorobutadiene and benzoquinone (Du Pont, U.S.P. 1967862). Hexachloro- $\alpha$ -naphthaquinone (m.p. 222–222.5°) is obtained from octachloronaphthalene by oxidation with nitric acid (Schvemberger and Gordon, A, 1934, 1357).

The most important chloro derivative is 2:3-dichloro- $\alpha$ -naphthaquinone, golden-yellow needles, m.p. 196°. It was first prepared by nitric acid oxidation of naphthalene tetrachloride, m.p. 182° (Helbig, Ber. 1895, 28, 505) but is most easily prepared from  $\alpha$ -naphthol by sulphonation followed by oxidation with chlorate and hydrochloric acid and the crude product chlorinated in hot acetic acid solution (Üllmann and Ettisch, *ibid.* 1921, 54 [B], 259). It may be conveniently prepared also by chlorinating 4-amino- $\alpha$ -naphthol hydrochloride in acetic acid solution (Zincke and Cooksey, Annalen, 1889, 255, 372) or by the action of thionyl chloride on 1:4-dihydroxy-3-naphthylpyridinium chloride (Koenigs and Greiner, Ber. 1931, 64 [B], 1045). It is also obtained by action of hydrogen chloride in ether on 4-nitroso- $\alpha$ -naphthol (Angeletti and Pirona, A, 1939, II, 58). It is insoluble in water, soluble in hot alcohol but sparingly so in cold. With boiling aqueous caustic soda it gives 3-chloro-2-hydroxy- $\alpha$ -naphthaquinone (Graebe, Annalen, 1869, 149, 3), and with aniline 3-chloro-2-anilino- $\alpha$ -naphthaquinone, the second chlorine group being non-reactive (Schultz, *ibid.* 1881, 210, 189). If, however, the 2-anilino-group is acetylated, the 3-chloro-group becomes mobile and can be replaced readily by amines (Fries and Billig, Ber. 1925, 58 [B], 1128) giving derivatives of 2:3-diamino- $\alpha$ -naphthaquinone, or by mercaptyl groups to give products useful as dye components (Höchst, G.P. 386998). 2:3-Dichloro- $\alpha$ -naphthaquinone reacts with oxythionaphthen to give vat dyestuffs (Kalle, G.P. 197037).

(iii) 2:6-Naphthaquinone, obtained by oxidation of 2:6-dihydroxynaphthalene with lead peroxide, forms reddish-yellow prisms and is odourless and non-volatile. Unlike [ $\beta$ ]-naphthaquinone, it is an oxidising agent comparable with *p*-benzoquinone (Willstätter and Parnas, Ber. 1907, 40, 1411, 3971).

#### HYDROXYNAPHTHAQUINONES.

(i) 2-Hydroxy- $\alpha$ -naphthaquinone can be obtained by acid or alkaline hydrolysis of 2-amino- $\alpha$ -naphthaquinone (Graebe and Ludwig, Annalen, 1870, 154, 321; Diehl and Merz, Ber. 1878, 11, 1315) or by acid hydrolysis of 2-anilino- $\alpha$ -naphthaquinone (Baltzer, *ibid.* 1881, 14, 1900). It is produced by air oxidation of an alkaline solution of [ $\beta$ ]-naphthaquinone-4-sulphonate (Kowalski, *ibid.* 1892, 25, 1659). It is also obtained by dissolving [ $\beta$ ]-naphthaquinone-4-sulphonic acid in sulphuric acid and finally pouring on to ice (Aktienges., B.P. 26675, 1897), but according to Fieser (J. Amer. Chem.

Soc. 1926, 48, 2922) the resulting product is a mixture of 2-hydroxy-[ $\alpha$ ]-naphthaquinone and 4-hydroxy-[ $\beta$ ]-naphthaquinone. According to Fieser and Martin (Organic Syntheses, Vol. XXI, p. 56) the most convenient method of preparation is to oxidise 1-amino-2-naphthol-4-sulphonic acid to [ $\beta$ ]-naphthaquinone-4-sulphonic acid which by reaction with sulphuric acid in methyl alcohol gives the methyl ether of 2-hydroxy-[ $\alpha$ ]-naphthaquinone, easily hydrolysed with boiling dilute caustic soda to 2-hydroxy-[ $\alpha$ ]-naphthaquinone, the overall yield being 46%. The product so obtained is in bright yellow granular form and for most purposes is sufficiently pure (m.p. 188–189°).

**Identification.**—It crystallises from alcohol or sublimates in yellow needles, m.p. 191–192°, dissolves only sparingly in boiling water, decomposes carbonate, and dyes wool or silk yellow. The acetate, yellow scales, has m.p. 130° (Thiele and Winter, *Annalen*, 1900, 311, 347).

**Reactions.**—It couples with diazo-compounds in acetic acid solution to give azo-dyes, the azo-group entering the 3-position (Kehrmann and Goldenberg, *Ber.* 1897, 30, 2126), but in an alkaline medium nitrogen is eliminated to give a 3-aryl-2-hydroxy-[ $\alpha$ ]-naphthaquinone (Neunhoeffer and Weise, *ibid.* 1938, 71 [B], 2703). Reduction with tin and hydrochloric acid gives 1:2:4-trihydroxynaphthalene. With *o*-phenylenediamine it behaves as if it were 4-hydroxy-[ $\beta$ ]-naphthaquinone, giving an azine (Kehrmann, *ibid.* 1890, 23, 2453; cf. Miller, *J.C.S.* 1911, 100, i, 465). In this connection it may be noted that [ $\alpha$ ]- and [ $\beta$ ]-naphthaquinones differ in absorption spectra only when substituent hydroxyl groups are absent (Beck, Maebeth, and Winzor, *A.* 1935, 347).

3- Nitro - 2 - hydroxy - [ $\alpha$ ]-naphthaquinone is formed by nitrating [ $\beta$ ]-naphthaquinone-4-sulphonic acid or 1-amino-2-naphthol-4-sulphonic acid in sulphuric acid below 50° (Aktienges., B.P. 26675, 1897). It is a crystalline product giving a yellow azo-dye with phenylhydrazine-sulphonic acid (Aktienges., G.P. 102071; B.P. 676, 1898).

2 - Hydroxy - [ $\alpha$ ]-naphthaquinone - 3 - sulphonic acid is formed by sulphonating 2-hydroxy-[ $\alpha$ ]-naphthaquinone with 25% oleum at 20° (Aktienges., G.P. 99759; B.P. 26675, 1897) and gives azo-dyes for wool by interaction with phenylhydrazinesulphonic acid (Aktienges., G.P. 101918; B.P. 676, 1898) or with the hydrazine from 1-amino-8-naphthol-3:6-disulphonic acid (Aktienges., G.P. 102070; B.P. 676, 1898).

2 - Hydroxy - [ $\alpha$ ]-naphthaquinone - 6 - sulphonic acid is obtained by maintaining a mixture of [ $\beta$ ]-naphthaquinone-4:6-disulphonic acid and sulphuric acid at 20° for several hours (Aktienges., G.P. 100703; B.P. 26675, 1897) or by oxidation of 1:2-dihydroxynaphthalene-6-sulphonic acid in caustic soda by hydrogen peroxide (Teichner and Weil, *Ber.* 1905, 38, 3376).

2 - Hydroxy - [ $\alpha$ ]-naphthaquinone - 7 - sulphonic acid (Gaess, *ibid.* 1899, 32, 237) forms an azine with *o*-phenylenediamine, reacting as if it were 4-hydroxy-[ $\beta$ ]-naphthaquinone-7-sulphonic acid.

(ii) 5-Hydroxy-[ $\alpha$ ]-naphthaquinone (*juglone*; *regianin*; *nucin*) occurs in the green part

of walnut shells (Brissemoret and Combes, *Compt. rend.* 1905, 141, 838; Combes, *Bull. Soc. chim.* 1907, [iv], 1, 803), but in nuts not freshly gathered is replaced wholly or partly by hydrojuglone (Mylius, *Ber.* 1885, 18, 2567). It may be prepared by oxidation of 1:4:5-trihydroxynaphthalene (hydrojuglone) with ferric chloride (Mylius, *l.c.*), or chromic acid (Bornthsen and Semper, *ibid.* 1885, 18, 204) or by oxidation of 1:5-dihydroxynaphthalene with chromic acid mixture (*idem*, *ibid.* 1887, 20, 939; Willstätter and Wheeler, *ibid.* 1914, 47, 2798) or by oxidation of 4:8-diamino- $\alpha$ -naphthol with ferric chloride (Friedländer and Silberstein, *Monatsh.* 1902, 23, 517). It is interesting to note that the chroming of Diamond Black PV (*o*-aminophenolsulphonic acid—1:5-dihydroxynaphthalene) gives the chromium lake of the corresponding juglone derivative (*v.* Vol. IV, 211c).

**Identification and Reactions.**—It crystallises in yellowish-red or brown needles, m.p. 151–154°, almost insoluble in water, and its aqueous solution, like walnut juice, stains the skin yellow. Chlorination in acetic acid gives 2:3-dichlorojuglone, orange needles, m.p. 149°, in which the 2-chlorine atom is easily replaced by the hydroxyl or arylamino group (Wheeler, Dawson, and MeEwen, *J. Amer. Chem. Soc.* 1923, 45, 1970). The tribromo derivative dyes silk and wool (Wheeler and Scott, *ibid.* 1910, 41, 835).

(iii) 6-Hydroxy-[ $\beta$ ]-naphthaquinone, m.p. 165° (decomp.), is obtained by oxidising 1-amino-2:6-dihydroxynaphthalene with ferric chloride (Kehrmann, *Ber.* 1907, 40, 1962).

Its 4-sulphonic acid is obtained by interaction of 1-nitroso-2:6-dihydroxynaphthalene with bisulphite and oxidation of the resulting product (Bayer, G.P. 87900; B.P. 6035, 1893).

(iv) 7-Hydroxy-[ $\beta$ ]-naphthaquinone, m.p. 194°, is obtained by oxidising 1-amino-2:7-dihydroxynaphthalene (Clausius, *Ber.* 1890, 23, 522; Nietski and Knapp, *ibid.* 1897, 30, 1123).

Its 4-sulphonic acid is obtained in brown needles by oxidising 1-amino-2:7-dihydroxynaphthalene-4-sulphonic acid with nitrous acid (Böniger, *ibid.* 1894, 27, 3051; Bayer, G.P. 87900; B.P. 6035, 1893).

(v) 8-Hydroxy-[ $\beta$ ]-naphthaquinone is not known, but its 6-sulphonic acid is obtained by oxidation of 8-hydroxy-1:2-diaminonaphthalene-6-sulphonic acid (Bayer, *l.c.*).

(vi) 2:3-Dihydroxy - [ $\alpha$ ]-naphthaquinone (*isonaphthazarin*) is formed when 3-amino-2-hydroxy-[ $\alpha$ ]-naphthaquinone is heated with dilute hydrochloric acid at 180° (Diehl and Merz, *Ber.* 1878, 11, 1322); from 1:4-diamino-2:3-dihydroxynaphthalene with ferric chloride (Friedländer and Silberstein, *Monatsh.* 1902, 23, 525); from [ $\beta$ ]-naphthaquinone by oxidation with hypochlorous acid (Zineke and Ossensbeck, *Annalen*, 1899, 307, 11; cf. Bamberger, *Ber.* 1892, 25, 134, 891; Zineke and Scharfenberg, *ibid.*, p. 409).

**Identification.**—It crystallises in red needles, m.p. 280°, and dissolves with a blue colour in caustic alkali, oxidising with air to colourless *o*-carboxyphenylglyoxylic acid. It is reduced to

either 1:2:3-trihydroxy- or 1:2:3:4-tetrahydroxynaphthalene, dependent on the vigour of reduction. Its diacetate forms colourless needles, m.p. 105° (Zincke and Ossenbeck, l.c.).

(vii) 5:6-Dihydroxy-[ $\alpha$ ]-naphthaquinone (orthonaphthazarin). Naphthazarin (v.i.) was once thought to have this constitution. 5:6-Dihydroxy-[ $\alpha$ ]-naphthaquinone was first synthesised by Dimroth and Roos (Annalen, 1927, 456, 177) as part of their investigation into the constitution of naphthazarin. It was formed by nitration and reduction of 6-hydroxy-[ $\alpha$ ]-naphthaquinone to give 5-amino-6-hydroxy- $\alpha$ -naphthaquinone which by ferric chloride oxidation gave orthonaphthazarin. Although similar in appearance to naphthazarin, it has inferior dyeing properties.

(viii) 5:8-Dihydroxy-[ $\alpha$ ]-naphthaquinone (Naphthazarin) was first prepared by Roussin (Compt. rend. 1861, 52, 1033, 1177) by heating 1:5-dinitronaphthalene with zinc and sulphuric acid at 200°. For many years its constitution was believed to be 5:6-dihydroxy-[ $\alpha$ ]-naphthaquinone, but the work of Dimroth and Ruck (Annalen, 1925, 446, 123), supported later by the evidence of Pfeiffer (Ber. 1927, 60 [B], 111) and Zahn and Ochwat (Annalen, 1928, 462, 81), showed that naphthazarin is 5:8-dihydroxy-[ $\alpha$ ]-naphthaquinone. The proof of constitution depends on the fact that it forms only a monoborate and does not give an azine with *o*-phenylenediamine.

**Preparation.**—The following process, described by Fierz-David and Stockar (Helv. Chim. Acta, 1943, 26, 92), is claimed to give a 59% yield; it is a modification of that of Bayer (G.P. 71386). 1:5-Dinitronaphthalene (20 g.) is dissolved in 400 g. of monohydrate and a solution of 7 g. of sulphur in 120 g. of 66% anhydrosulphuric acid added with cooling, the temperature being kept below 40°. After stirring for 30 minutes, the mixture is poured on to 500 g. of ice, filtered, and the filtrate boiled. The filtered, washed, and dried naphthazarin can be sublimed at 170–180° in a vacuum.

Other patents have described the preparation in which hydrogen sulphide or sulphur chloride is used instead of sulphur (Bayer, G.P. 77330; B.P. 17673, 1892); it has also been stated that naphthazarin can be prepared from 1:8-dinitronaphthalene (Badische, G.P. 76922; 79406; B.P. 3828, 1894). Fierz-David and Stockar (l.c.), however, obtained no trace of naphthazarin from the 1:8-isomer by their method, but a smaller amount was formed when aniline was added to the mixture.

**Properties.**—Naphthazarin sublimes in brown needles with green lustre, is sparingly soluble in water but soluble in alkali giving a cornflower-blue solution and in sulphuric acid giving a magenta solution. It reacts with phenylhydrazine to give a benzeneazo derivative of trihydroxynaphthalene (Charrier and Tocco, Gazzetta, 1923, 53, 431). It is a mordant dye-stuff giving violet-black lakes on chrome mordant, and is more important as the solubilised derivative (Alizarin Black S) obtained by reaction with sodium bisulphite (Badische, G.P. 41518; B.P. 7835, 1887). Reaction with sodium bisulphite at 100° followed by oxidation

of the resulting leuco-compound gives naphthazarinsulphonic acid (Höchst, G.P. 116866). The diacetate of naphthazarin has m.p. 189° (Zincke and Schmidt, Annalen, 1895, 286, 36).

Condensation of naphthazarin with salts of aromatic amines or their sulphonic acids in presence of boric acid gives black dyestuffs (Badische, B.P. 21297, 1897; 2468, 1904; cf. Fierz-David and Stockar, l.c.).

The naphthazarin melt contains a "naphthazarin intermediate product," the blue solution of which in water, when boiled, gives naphthazarin. It can be isolated by a number of methods (Höchst, G.P. 111683; B.P. 16295, 1899; Badische, G.P. 108551–2; 101372; B.P. 15709, 1898; cf. Bayer, G.P. 104282; 105567). This intermediate product has been widely investigated by dyestuff firms as a source of dyestuffs.

(ix) 6:7-Dihydroxy-[ $\alpha$ ]-naphthaquinone formed by ferric chloride oxidation of 5-amino-2:3:8-trihydroxynaphthalene has only feeble dyeing properties. Its diacetate forms yellow needles, m.p. 65–67° (Friedländer and Silberstein, Monatsh. 1902, 23, 532).

(x) 5:6:8-Trihydroxy-[ $\alpha$ ]-naphthaquinone (naphthapurpurin) is obtained by boiling naphthazarin with an equal weight of caustic soda in 1% solution until the colour changes to magenta (Badische, G.P. 167641; B.P. 9547, 1905) or with manganese dioxide and dilute sulphuric acid (Jaubert, Compt. rend. 1899, 129, 684). It forms reddish-brown needles, easily soluble in solvents, dyes wool orange-red chroming to black (Badische, l.c.), and when condensed with amines and sulphonated gives dyestuffs for chromed wool (Bayer, G.P. 127766).

#### NAPHTHAQUINONESULPHONIC ACIDS.

(i) [ $\beta$ ]-Naphthaquinone-4-sulphonic Acid is obtained by oxidation of 2-amino-1-naphthol-4-sulphonic acid (Witt and Kaufmann, Ber. 1891, 24, 3163) or 1-amino-2-naphthol-4-sulphonic acid with nitric acid. The latter method is fully described by Martin and Fieser (Organic Syntheses, Vol. XXI, p. 91). In brief, 300 g. of pure anhydrous 1-amino-2-naphthol-4-sulphonic acid is added in portions to a mixture of 145 c.c. nitric acid ( $\rho$  1.42) and 400 c.c. water at 25–30°. The finished thick reaction mass is diluted with 175 c.c. saturated ammonium chloride solution, the mixture cooled to 0° and the ammonium salt of [ $\beta$ ]-naphthaquinone-4-sulphonic acid filtered, washed with ammonium chloride solution and finally with alcohol and ether, and dried at 35–40°. The yield is 94–98% and the product pure enough for most purposes. It may be purified by conversion to the potassium salt.

**Reactions.**—On nitration it yields 3-nitro-2-hydroxy-[ $\alpha$ ]-naphthaquinone and with sulphuric acid at 25° a mixture of 2-hydroxy-[ $\alpha$ ]-naphthaquinone and 4-hydroxy-[ $\beta$ ]-naphthaquinone (Fieser, J. Amer. Chem. Soc. 1926, 48, 2922). Reduction by sulphurous acid gives 1:2-dihydroxynaphthalene-4-sulphonic acid. Condensation with aromatic nitroso-compounds in presence of thiosulphate gives thiazines with elimination of the sulphonic group (Bayer, G.P. 83046); with aminonaphtholsulphonic acids followed by oxidation it gives oxazines (Dahl, G.P. 82740; B.P. 5153, 1895).

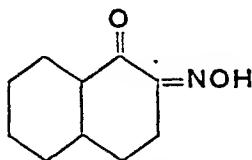
[ $\beta$ ]-Naphthaquinone-6-, 7-, and 8-mono- and 4:6-, 4:7-, and 4:8-di-sulphonic acids have been obtained by oxidising the corresponding amino- $\beta$ -naphtholsulphonic acids and used in the preparation of thiazine dyestuffs (Bayer, G.P. 84233; B.P. 4757, 1893; Sandoz, G.P. 116765).

(ii) [ $\alpha$ ]-Naphthaquinone-2-sulphonic Acid is obtained by nitric acid oxidation of 4-amino-1-naphthol-2-sulphonic acid (Conrad and Fischer, *Annalen*, 1893, 273, 115) and by the action of potassium bisulphite on [ $\alpha$ ]-naphthaquinone followed by oxidation with dichromate (Fieser and Fieser, J. Amer. Chem. Soc. 1935, 57, 491). It has been used in the preparation of vat dyestuffs (Kalle, G.P. 286151).

#### NAPHTHAQUINONEOXIMES.

Of the three naphthaquinoneoximes the only technically important one is [ $\beta$ ]-naphthaquinone-1-oxime (nitroso- $[\beta]$ -naphthol).

(i) 2-Nitroso- $\alpha$ -naphthol ([ $\beta$ ]-naphthaquinone-2-oxime),



is obtained from [ $\beta$ ]-naphthaquinone and hydroxylamine hydrochloride (Goldschmidt, *Ber.* 1884, 17, 215); or from 1-hydroxy- $\beta$ -naphthoic acid by action of nitrous acid (Reverdin and de la Harpe, *ibid.* 1893, 26, 1280); or mixed with the 4-oxime by action of nitrous acid on  $\alpha$ -naphthol (Henriques and Ilinski, *ibid.* 1885, 18, 706). It is also a product of the reaction of methyl alcoholic potash with  $\beta$ -nitronaphthalene. It crystallises in yellow needles, m.p. 152°, soluble in hot water and most solvents, forms green potassium and ammonium salts and greenish-yellow methyl and ethyl ethers (Fuchs, *ibid.* 1875, 8, 626).

**Reactions.**—With concentrated nitric acid in acetic acid solution it produces 2:4-dinitro- $\alpha$ -naphthol; potassium ferricyanide oxidises it to 2-nitro- $\alpha$ -naphthol. With sodium bisulphite it yields 2-amino-1-naphthol-4-sulphonic acid. When boiled with aniline and acetic acid it gives 2-anilino- $[\alpha]$ -naphthaquinoneanil as do 4-nitroso- $\alpha$ -naphthol and 1-nitroso- $\beta$ -naphthol (Brömme, *ibid.* 1888, 21, 393). Like nitroso- $\beta$ -naphthol, with hydroxylamine it gives [ $\beta$ ]-naphthaquinone-dioxime (Goldschmidt and Schmid, *ibid.* 1884, 17, 2066), yields metallic salts (Ilinsky, *ibid.* 1884, 17, 2589), and is a mordant dye known as Gambine-R (cf. Aktienges., G.P. 66786).

2-Nitroso- $\alpha$ -naphthol-4-sulphonic acid gives a Naphthol Green with ferric chloride (Gans & Co., G.P. 28065; B.P. 2269, 1884; Hoffmann, *Ber.* 1885, 18, 46).

(ii) 4-Nitroso- $\alpha$ -naphthol ([ $\alpha$ ]-naphthaquinone-4-oxime) is formed when [ $\alpha$ ]-naphthaquinone interacts with hydroxylamine hydrochloride (Goldschmidt and Schmid, *ibid.* 1884, 17, 2064); or, mixed with [ $\beta$ ]-naphthaquinone-2-oxime, by the action of nitrous acid on  $\alpha$ -naphthol. The latter reaction is carried out in alcohol using zinc chloride and sodium nitrite and gives from 100 g.  $\alpha$ -naphthol, 40 g. of

[ $\alpha$ ]-naphthaquinone-4-oxime and 50 g. of [ $\beta$ ]-naphthaquinone-2-oxime (Henriques and Ilinski, *ibid.* 1885, 18, 706). It crystallises in needles, m.p. 190° (Friedländer and Reinhardt, *ibid.* 1894, 27, 240), dissolves easily in alcohol or ether, gives a methyl ether, m.p. 98–100° (Ilinski, *ibid.* 1884, 17, 2590), and has no tinctorial power (Kostanecki, *ibid.* 1887, 20, 3147).

**Reactions.**—With concentrated nitric acid it gives 2:4-dinitro- $\alpha$ -naphthol; with potassium ferricyanide, 4-nitro- $\alpha$ -naphthol. Reduction with stannous chloride converts it into 4-amino- $\alpha$ -naphthol. Heated with aniline and acetic acid it gives 2-anilino- $[\alpha]$ -naphthaquinoneanil as do 2-nitroso- $\alpha$ -naphthol and 1-nitroso- $\beta$ -naphthol (Brömme, *ibid.* 1888, 21, 393). With hydrogen chloride in ether it gives 2:3-dichloro- $[\alpha]$ -naphthaquinone (Angeletti and Pirona, A. 1939, II, 58).

The 2-sulphonic acid is converted to 2:4-dinitro- $\alpha$ -naphthol by nitric acid (Conrad and Fischer, *Annalen*, 1893, 273, 110).

The 2:5-disulphonic acid, formed by action of concentrated caustic soda solution on  $\alpha$ -nitronaphthalene-3:8-disulphonic acid, forms a yellow potassium salt,  $K_2A + 1\frac{1}{2}H_2O$ , and a green basic potassium salt. Reduction gives 4-amino-1-naphthol-2:5-disulphonic acid (Friedländer, *Ber.* 1895, 28, 1535).

**Nitro Derivatives.**—5-Nitro-4-nitroso- $\alpha$ -naphthol (5-nitro- $[\alpha]$ -naphthaquinone-4-oxime) produced by heating 1:8-dinitronaphthalene with 12–23% anhydro-acid at 40–50°, crystallises in yellow needles, soluble in alkali to give a yellow solution becoming red when heated with zinc dust (Badische, G.P. 90414; B.P. 14955, 1896; Graebe, *ibid.* 1899, 32, 2877; Friedländer, *ibid.*, p. 3528; Friedländer and Scherzer, cf. J.S.C.I. 1900, 19, 339). With potassium ferricyanide it gives 4:5-dinitro- $\alpha$ -naphthol; with nitric acid 2:4:5-trinitro- $\alpha$ -naphthol, and with permanganate 3-nitrophthalic acid. Reduced by ammonium sulphide or stannous chloride it gives 4:5-diamino- $\alpha$ -naphthol, but with tin and hydrochloric acid 5-amino-1:4-dihydroxynaphthalene. Its 2:7-disulphonic acid, obtained by action of dilute caustic soda on 1:8-dinitronaphthalene-3:6-disulphonic acid at ordinary temperature, gives a yellow potassium salt,  $K_2A + 2H_2O$ , and a green basic potassium salt, and with dilute nitric acid one of the sulphonic groups is replaced by a nitro-group giving a nitro-dyestuff (Kalle, G.P. 113063).

7-Nitro-4-nitroso- $\alpha$ -naphthol (7-nitro- $[\alpha]$ -naphthaquinone-4-oxime) obtained by heating 1:6-dinitronaphthalene with 15–17% anhydro acid at 40–50° forms yellow needles, is soluble in alkalis and on oxidation gives 4-nitrophthalic acid (Graebe, *Annalen*, 1901, 335, 144).

8-Nitro-4-nitroso- $\alpha$ -naphthol (8-nitro- $[\alpha]$ -naphthaquinone-4-oxime) obtained by heating 1:5-dinitronaphthalene with 12–23% anhydro-acid at 40–50° (Badische, G.P. 91391; B.P. 14955, 1896) forms yellow needles dissolving in alkali to give a yellow solution which becomes green when boiled with zinc dust. It is oxidised by ferricyanide to 4:8-dinitro- $\alpha$ -naphthol but with dilute nitric acid gives 2:4:8-trinitro- $\alpha$ -naphthol. On reduction with tin and hydrochloric acid it yields 4:8-diamino- $\alpha$ -naphthol.

(iii) 1-Nitroso- $\beta$ -naphthol ([ $\beta$ ]-naphtha-

quinone-1-oxime) is obtained by the action of nitrous acid on  $\beta$ -naphthol (Fuchs, Ber. 1875, 8, 1026; Ilinski, Ber. 1884, 17, 2584; Groves, J.C.S. 1884, 45, 295; cf. Köhler, G.P. 25469). Its preparation is fully described by Marvel and Porter (Organic Syntheses, Vol. II, p. 60). In brief, 500 g.  $\beta$ -naphthol is dissolved in a solution of 140 g. caustic soda in 6 litres of water, cooled to 0°, 250 g. sodium nitrite added followed by 1,100 g. sulphuric acid ( $\rho$  1.32) added over 1½ hours, the temperature being maintained at 0° by addition of ice. The reaction mass is stirred during 1 hour, filtered, and well washed. The light yellow precipitate is dried in the air for four days and finally in vacuum over sulphuric acid, the product (m.p. 106° and yield 99%) being pure enough for most purposes.

**Identification.**—It crystallises from alcohol in plates or prisms, m.p. 109-5°, is sparingly soluble in hot water and when pure is readily volatile in steam (Ilinski, Ber. 1884, 17, 2584). The cupric salt,  $\text{CuA}_2$  (Knorre, *ibid.* 1887, 20, 283), and ferric salt,  $\text{FeA}_3$ , are insoluble in water or 50% acetic acid and the cobaltic salt,  $\text{CoA}_2$ , is only slightly soluble in boiling 50% acetic acid. These properties can be used in the separation of copper, iron, or cobalt from other metals (cf. Knorre, Z. angew. Chem. 1893, 6, 264; Attack, J.S.C.I. 1915, 34, 641; Mayr and Feigl, Z. anal. Chem. 1932, 90, 15). The barium, potassium, and sodium salts are green (Ilinski, Ber. 1884, 17, 2885). The insoluble ferrous salt of nitroso- $\beta$ -naphthol is largely used as a green lake (Badische, G.P. 356973). The constitution of the iron compounds of nitroso- $\beta$ -naphthol is discussed on p. 380b.

**Reactions.**—By dilute nitric acid or ferricyanide it is oxidised to 1-nitro- $\beta$ -naphthol. Reduced with stannous chloride it gives 1-amino- $\beta$ -naphthol. In cold caustic soda solution with hydroxylamine it gives  $\beta$ -[naphthoquinone-dioxime], m.p. 180-181°, but if warm the anhydride, m.p. 78°, is formed (Kehrmann and Messinger, Ber. 1890, 23, 2815). Boiled with aniline and acetic acid it gives 2-anilino- $\alpha$ -[naphthoquinoneanil] (Brömme, *ibid.* 1888, 21, 393), but under milder conditions with aniline in benzene it gives 1-imino-2-hydroxy-4-phenyliminonaphthoquinone (Soc. Anon., B.P. 246482; cf. Lantz and Wahl, Bull. Soc. chim. 1929, [iv], 45, 744). When the sodium salt of 1-nitroso- $\beta$ -naphthol is heated alone, or better in pyridine or in aqueous caustic soda with a sulphonyl chloride, ring fission occurs and it is converted into sodium *o*-cyanocinnamate (Bayer, G.P. 116123; Werner and Piguet, Ber. 1904, 37, 4310; Weiler-ter Meer, G.P. 411955). Chlorination of 1-nitroso- $\beta$ -naphthol in tetrachloroethane with sulphuryl chloride is said to give 3-chloro-1-nitroso-2-naphthol, m.p. 168° (Marschalk, Bull. Soc. chim. 1928, [iv], 43, 1361). With aqueous potassium cyanide at 80-85° 1-nitroso- $\beta$ -naphthol gives 1-amino-2-hydroxy-4-cyanonaphthalene, m.p. 200-201° (I.C.I., B.P. 381602; cf. Bradley and Robinson, J.C.S. 1934, 1484). With sodium bisulphite solution it gives a crystalline bisulphite compound, the constitution of which has been studied by Bogdanov (A. 1932, 842, and A. 1933, 389) and is used as a mordant dye under the name Fast Printing Green. The

bisulphite compound, unlike nitroso- $\beta$ -naphthol, couples with diazo-compounds to give azo-dyes, but these have no commercial value (Dahl, G.P. 79583; 95758; Ashworth and Bürger, B.P. 11556, 1893). The most valuable reaction of the bisulphite compound is its conversion by mineral acid to 1-amino-2-naphthol-4-sulphonic acid (Böniger, Ber. 1894, 27, 23; cf. Fieser, Organic Syntheses, Vol. XI, p. 12; Vol. XXI, p. 94). Nitroso- $\beta$ -naphthol has been proposed as a plasticising agent for rubber (Du Pont, F.P. 816395); under the name Gambine-Y it is used as mordant dyestuff (Robinson, J. Soc. Dyers and Col. 1921, 37, 229).

1-Nitroso-2-naphthol-6-sulphonic acid obtained by action of nitrous acid on  $\beta$ -naphthol-6-sulphonic acid (Meldola, J.C.S. 1881, 39, 40) gives an orange barium salt, a green basic barium salt and a green basic sodium salt (Hoffmann, Ber. 1891, 24, 3741). With cobalt, nickel, and iron, co-ordinated compounds are formed, the iron complex (Naphthol Green-B) being a dyestuff for wool (Gans, G.P. 28065; 28901; cf. Ulrich, J.S.C.I. 1890, 9, 1126).

The 3:6-disulphonic acid, obtained by the action of nitrous acid on  $\beta$ -naphthol-3:6-disulphonic acid can be used as a sensitive test for cobalt (Van Klooster, J. Amer. Chem. Soc. 1921, 43, 746).

1-Nitroso-2:6-dihydroxynaphthalene (Bayer, B.P. 14230, 1889); 1-nitroso-2:7-dihydroxynaphthalene, known as Gambine-B (Leonhardt, B.P. 17223, 1889); and nitroso-2:8-dihydroxynaphthalene (Bayer, B.P. 14230, 1889) have been used as mordant dyes.

## ARYLNAPHTHALENES.

The phenylnaphthalenes, or naphthylbenzenes, have been prepared by several different methods. They are not at present of technical importance.

$\alpha$ -Phenylnaphthalene is a liquid, b.p. 324-325° (Möhlau and Berger, Ber. 1893, 26, 1196; Chattaway, J.C.S. 1893, 63, 1186), b.p. 334°/770 mm. (R. Weiss and K. Woidich, Monatsh. 1925, 46, 453). Chattaway, who obtained it, with some of the  $\beta$ -isomer, by the interaction of  $\alpha$ -chloronaphthalene and benzene in presence of aluminium chloride, described it as a soft waxy solid of indefinite m.p. up to 45°, but other authors have not obtained it in solid form. Möhlau and Berger separated it by fractional distillation of the mixed  $\alpha$ - and  $\beta$ -isomers obtained from diazobenzene and naphthalene. Weiss and Woidich synthesised it from 1-ketotetrahydronaphthalene and phenyl magnesium bromide, and T. Wagner-Jauregg from *as*-diphenylethylene and maleic anhydride (Annalen, 1931, 491, 1). Grieve and Hey obtained it in small yield from diazotised  $\alpha$ -naphthylamine and benzene (J.C.S. 1938, 108).

According to F. Mayer and R. Schiffner,  $\alpha$ -phenylnaphthalene changes to  $\beta$ -phenylnaphthalene at 350° in contact with silica or silicates (Ber. 1934, 67 [B], 67).

$\alpha$ -Phenylnaphthalene can be characterised by nitration in acetic acid to a mononitro derivative, m.p. 135° (*idem, ibid.*; Weiss and Woidich, *l.c.*,



give m.p. 132°), which, according to V. Veselý and F. Štursa is 4-nitro-1-phenylnaphthalene (Coll. Czech. Chem. Comm. 1933, 5, 343). These authors describe 4-amino-1-phenylnaphthalene, m.p. 73-74° (acetyl derivative, m.p. 167-168°), and other derivatives. Methoxy derivatives of 1-phenylnaphthalene have been described by W. N. Howell and A. Robertson (J.C.S. 1936, 587).

$\beta$ -Phenylnaphthalene has m.p. 101-102° (Möhlau and Berger, *l.c.*; Hey and Laughton, *ibid.* 1940, 374). The best preparative method appears to be that described by Hey and Laughton, from nitrosoacet- $\beta$ -naphthalide and benzene. These authors prepared some of its substitution derivatives by the same method. Nitration of 2-phenylnaphthalene gives the 1-nitro-compound, m.p. 127°; 2-phenyl- $\alpha$ -naphthylamine has m.p. 104° (acetyl derivative, m.p. 234°).

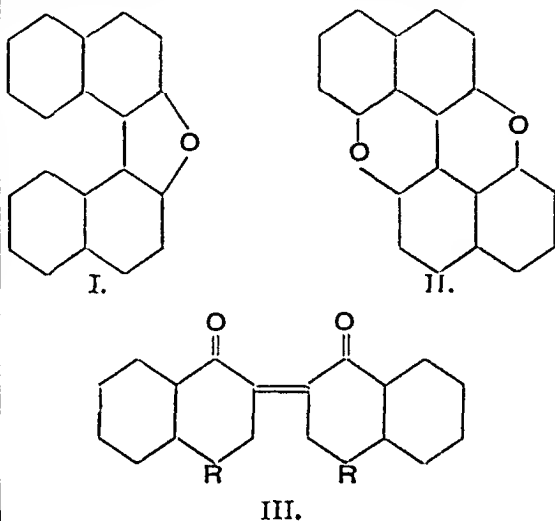
$\beta$ -Phenylnaphthalene has also been synthesised from diphenyl and succinic anhydride (Hey and Wilkinson, *ibid.* 1940, 1030; Weizmann, Bergmann, and Bograchov, Chem. and Ind. 1940, 59, 402); from deoxybenzoin and ethyl bromoacetate (F. S. Spring, J.C.S. 1934, 1332), and from  $\alpha$ -amino- $\beta$ -methoxy- $\beta$ -phenylpropionic acid (Carter and Van Loon, J. Amer. Chem. Soc. 1938, 60, 1077). By the action of aromatic diazo-compounds in alkaline solution on 2-hydroxy-[ $\alpha$ ]naphthaquinone (O. Neunhoeffer and J. Weise, Ber. 1938, 71 [B], 2703), 2-hydroxy-3-aryl-[ $\alpha$ ]naphthaquinones are obtained.

Diphenylnaphthalenes and some of their derivatives have been obtained by synthetic methods involving formation of the naphthalene ring. A specially interesting example is the reaction between diphenylketone,  $\text{C}_6\text{H}_5\text{CO}$ , and phenylacetylene, which takes place at room temperature, to give 3:4-diphenyl- $\alpha$ -naphthol, m.p. 143-144°. The reaction has been studied in some detail by L. I. Smith and H. H. Hoehn, who show that the aryl group in the arylacetylene is found in the 3-position in the 3:4-diaryl- $\alpha$ -naphthol. The last compound is also obtained from [ $\alpha$ ]naphthaquinone and phenyl magnesium bromide (J. Amer. Chem. Soc. 1939, 61, 2619; 1941, 63, 1175). H. M. Crawford has synthesised 1:2-, m.p. 109.5-110°, 1:3-, m.p. 70-71°, and 2:3-diphenylnaphthalene, m.p. 86-87° (*ibid.* 1939, 61, 608); whilst F. Bergmann, H. E. Eschinarzi and D. Schapiro have prepared 1:2-diphenylnaphthalene, m.p. 114° (picrate, 148°), and 1:2:3-triphenylnaphthalene, m.p. 153° (*ibid.* 1942, 64, 557, 559). 1:4-Diphenylnaphthalene has m.p. 135-137° (Weiss, Abeles, and Knapp, Monatsh. 1932, 61, 162; Dufraisse and Priou, Bull. Soc. chim. 1938, [v], 5, 502). 2:6-Diphenylnaphthalene has m.p. 233-234° (Price and Tomisek, J. Amer. Chem. Soc. 1943, 65, 439).

#### DINAPHTHYL COMPOUNDS.

Dinaphthyl compounds have been the subject of patents by industrial firms, both for their preparation and for their use as intermediate compounds. Three series of compounds are known, derived respectively from 1:1'-, 2:2'-, and

1:2'-dinaphthyl. The most important compounds technically are the 1:1'-dinaphthyl-8:8'- and 2:2'-dicarboxylic acids, since they furnish by ring closure the important vat dyestuff anthranthrono (G.P. 280787, 1918; Kalb, Ber. 1914, 47, 1724). (v. Vol. I, 426a).  $\beta\beta'$ -Dinaphthol (2:2'-di-hydroxy-1:1'-dinaphthyl) is readily converted into the hydrocarbon perylene, which has been extensively investigated, though without technical success, as a possible intermediate for vat dyes.  $\beta\beta'$ -Dinaphthol also gives by dehydration dinaphthylene oxide (I), and by oxidation dinaphthylene dioxide (II); the latter can be halogenated and oxidised to quinones which have been claimed as useful colouring matters (I.G., B.P. 298610; 323806; 324017; 337061; G.P. 501324).



Related to 2:2'-dinaphthyl are the indigoid dyes of type (III) ( $\text{R}=\text{OMe}$ ,  $\text{Br}$ , etc.) obtainable by oxidising 4-methoxy- $\alpha$ -naphthol (Russig, J. pr. Chem. 1900, [ii], 62, 53) and from 2:4-dibromo- $\alpha$ -naphthol (Willstätter and Schnler, Ber. 1928, 61 [B], 362; Goldschmidt and Wessbecher, *ibid.*, p. 372).

1:1'-Dinaphthyl, m.p. 160.5°, has been obtained by oxidation, pyrolysis or catalytic dehydrogenation of naphthalene (Smith, J.C.S. 1877, 32, 559; 1879, 35, 225; Meyer and Hoffman, Monatsh. 1916, 37, 708; I.G., B.P. 356189) and by the action of metals on  $\alpha$ -halogenonaphthalenes. It is probably best prepared by heating  $\alpha$ -iodonaphthalene with copper bronze (Ullmann and Bielecki, Ber. 1901, 34, 2184; cf. Willgerodt and Schlösser, *ibid.* 1900, 33, 698; Späth, Monatsh. 1913, 34, 2013).

It is converted into perylene by heating with aluminium chloride at 140° (Scholl, Seer, and Weitzenböck, Ber. 1910, 43, 2204) and is said to be isomerised to  $\beta\beta'$ -dinaphthyl by aluminium chloride in carbon disulphide (Weitzenböck, quoted by Scholl and Tritsch, Monatsh. 1911, 32, 998, footnote). On nitration it gives mainly 4-nitro- and 4:4'-dinitro-compounds (Schoepfle, J. Amer. Chem. Soc. 1923, 45, 1567).

2:2'-Dihydroxy-1:1'-dinaphthyl, m.p. 218°, insoluble in water, soluble in alcohol and ether, is readily obtained in good yield by oxidising  $\beta$ -naphthol with hot aqueous ferric chloride and hydrochloric acid, or by the Ull



mann reaction from 1-bromo- $\beta$ -naphthol (cf. Hinsberg, Ber. 1915, 48, 2095).

Sulphonated, it gives the 6-mono- and 6:6'-disulphonic acids (Joffe, A. 1936, 1503). It is converted into perylene by halogen compounds of phosphorus at 400–500° (Hansging and Zinke, Monatsh. 1919, 40, 403; B.P. 136564), and into 1:12-dihydroxyperylene when heated with aluminium chloride (Pereira, B.P. 191363; cf. G.P. 390619; 391825; 394437). When it is distilled with zinc dust or heated with zinc chloride, dinaphthylene oxide is formed (Schoepfle, l.c.), and with zinc chloride and ammonia, *dinaphthyleneimine* (Walder, Ber. 1882, 15, 2166). It is converted into *dinaphthylene dioxide* by oxidation with silver oxide or sodium ferricyanide (Pummerer and Frankfurter, *ibid.* 1914, 47, 1493; cf. Pummerer, Prell, and Rieche, *ibid.* 1926, 59 [B], 2159) or by catalytic oxidation in presence of vanadium pentoxide (Clemo and Spence, J.C.S. 1928, 2812).

4:4'-Dihydroxy-1:1'-dinaphthyl, m.p. 301–302°, was first obtained by ferric chloride oxidation of  $\alpha$ -naphthol by Dianin (J. Russ. Phys. Chem. Soc. 1874, 6, 183) and its constitution proved by Clemo, Cockburn, and Spence (J.C.S. 1931, 1265). By dehydration it is converted into a *dinaphthylene oxide*, but isomerisation must first occur. Its *dimethyl ether* has m.p. 252° (Corbellini, Gazzetta, 1939, 59, 391).

2:7:2':7'-Tetrahydroxy-1:1'-dinaphthyl is obtained by oxidation of 2:7-dihydroxynaphthalene with ferric chloride (Brass and Patzelt, Ber. 1937, 70 [B], 1341).

2:2'-Diamino-1:1'-dinaphthyl, m.p. 191°, is formed when  $\beta$ -nitronaphthalene is reduced under conditions which might be expected to give the hydrazo-compound (Cumming and Ferrier, J.C.S. 1924, 125, 1109). Its *diacetyl* derivative has m.p. 235–236°. Heated at 240–250° it gives a dibenzocarbazole.

3:3'-Diamino-1:1'-dinaphthyl, m.p. 270°, was obtained by Cumming and Howie (*ibid.* 1932, 528) by reduction of the 3:3'-dinitro-compound (Chudžilov, Chem. Listy, 1925, 19, 187).

4:4'-Diamino-1:1'-dinaphthyl (*naphthidine*), m.p. 202°, is formed when  $\alpha$ -naphthylamine is oxidised with ferric iron in 88% sulphuric acid (Reverdin and de la Harpe, Chem.-Ztg. 1892, 16, 1687) and in small amount by the conversion of 1:1'-hydrazonaphthalene with hydrochloric acid, although the main product is 1:1'-diamino-2:2'-dinaphthyl (Nietzki and Goll, Ber. 1885, 18, 3254; cf. Veselý, *ibid.* 1905, 48, 136). It is also obtained from 4:4'-dinitro-1:1'-dinaphthyl, m.p. 246°, the principal product of dinitrating 1:1'-dinaphthyl (Schoepfle, J. Amer. Chem. Soc. 1923, 45, 1567), by reduction. Its *diacetyl* derivative has m.p. 363–364° (Cumming and Howie, l.c.). When the diamine or a salt thereof is heated with aluminium chloride it forms 3:10-diaminoperylene (Comp. Nat. de Mat. Col., B.P. 208720). Its tetrazo derivative is convertible into 4:4'-dihydroxy-1:1'-dinaphthyl (Corbellini, l.c.).

2:1'-Dinaphthyl, m.p. 79–80° (Wegscheider, Ber. 1890, 23, 3199) is obtained by passing naphthalene through a red hot tube (Smith,

J.C.S. 1877, 32, 560; 1879, 35, 227). Its *picrate* has m.p. 155–156°.

2:2'-Dinaphthyl, m.p. 187.8° (corr.), is obtained as one of the products by passing naphthalene through a red hot tube (Smith, l.c., cf. Meyer and Hofmann, Monatsh., 1916, 37, 708); or over a catalyst at 800° (I.G., B.P. 356189); or by action of copper powder on  $\beta$ -iodonaphthalene (Ullmann, and Gilli, Loewenthal and Meyer, Annalen, 1904, 332, 50); or from  $\beta$ -chloronaphthalene and sodium or from  $\beta$ -naphthylamine by diazotising and reacting in alcoholic solution with zinc and copper sulphate (Chattaway, J.C.S. 1895, 67, 656). It crystallises in blue fluorescent plates giving fluorescent solutions. It is only sparingly soluble in most solvents but is readily soluble in carbon disulphide, ethylene dibromide, and hot benzene. With chromic acid and acetic acid it is oxidised to the 1:4-quinone, accompanied by a little 1:4:1':4'-diquinone. By sulphonation with a deficiency of sulphuric acid at 200°, a *monosulphonic acid* has been obtained and with increased quantity of sulphuric acid two isomeric *disulphonic acids* are formed (Smith and Takamatsu, *ibid.* 1881, 39, 551).

1:1'-Diamino-2:2'-dinaphthyl is the main product of reaction of 1:1'-hydrazonaphthalene with hydrochloric acid (Nietzki and Goll, Ber. 1885, 18, 3254; Veselý, *ibid.* 1905, 48, 136). Heated with hydrochloric acid it loses ammonia with formation of dibenzocarbazole.

#### DINAPHTHYLDICARBOXYLIC ACIDS.

The dinaphthyl dicarboxylic acids which have attracted investigators are the 1:1'-dinaphthyl-2:2'- and 8:8'-dicarboxylic acids, both of which by cyclisation in sulphuric acid produce anthanthrone. They have been prepared (a) by heating the appropriate chloronaphthoic ester with copper bronze; (b) from the appropriate aminonaphthoic acid or ester by diazotising and treating the diazo-compound with ammoniacal cuprous oxide; (c) from 2:2'-diamino-1:1'-dinaphthyl through the tetrazo-compound and the dinitrile. The second is technically the most attractive procedure.

(i) 1:1'-Dinaphthyl-2:2'-dicarboxylic Acid has been obtained by methods (a) and (c) (Kalb, *ibid.* 1914, 47, 1724), and (b) I.G., B.P. 278100). The acid, m.p. 268.5–270°, has been resolved into optically active forms by means of the quinine salt (Kuhn and Albrecht, Annalen, 1928, 465, 285).

(ii) 1:1'-Dinaphthyl-8:8'-dicarboxylic Acid has been prepared by methods (a) and (b) (l.c.). The acid has m.p. above 300°, the *ethyl ester* m.p. 183°. The acid has been resolved into *d*- and *l*-forms (Corbellini, Atti. R. Accad. Lincei, 1931, 13, 702; Meisenheimer and Beisswenger, Ber. 1932, 65, 32).

In conclusion the writers must acknowledge their indebtedness to Professor W. P. Wynne, whose article in the 1922 edition of this Dictionary has been freely used. The general scheme of that article has been retained, and large sections of it have been preserved practically unchanged.

E. H. R., H. S., E. G. B., W. R. H. H.

## PART II. ALKYLNAPHTHALENES AND THEIR DERIVATIVES.

### SYNOPSIS OF THE SUBJECT.

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Higher Alkylated Naphthalenes (p. 390b).

Derivatives of  $\alpha$ -Methylnaphthalene (p. 393b); Halogeno Derivatives (p. 393b); Nitro Derivatives (p. 394a); Sulphonic Acids (p. 394d); Amino Derivatives (p. 395b); Hydroxy Derivatives (p. 396a).

Derivatives of  $\beta$ -Methylnaphthalene (p. 397a); Halogeno Derivatives (p. 397a); Nitro Derivatives (p. 397b); Sulphonic Acids (p. 397d); Amino Derivatives (p. 398a); Nitro-amines and Diamines (p. 398b); Hydroxy Derivatives (p. 398d); 2-Methylnaphthaquinones (p. 399a); Acyl Derivatives (p. 399d).

Ethyl-naphthalenes (p. 399d).

Propyl-naphthalenes (p. 401a).

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Dimethylnaphthalenes (p. 402c).

Trimethylnaphthalenes (p. 404a).

Polymethylnaphthalenes (p. 405b).

Naphthylacetic Acids and Homologues (p. 406b).

Naphthyl Alkyl Ketones (p. 406d).

Naphthyl Aryl Ketones (p. 408a).

Benzyl Derivatives of Naphthalene (p. 408d).

### $\alpha$ - AND $\beta$ -METHYLNAPHTHALENES.

Monomethylnaphthalenes and their higher homologues, which bear the same relation to naphthalene as toluene, the xylenes and their homologues to benzene, are present in the higher fractions of coal-tar distillates. F. Reingruber first isolated a fraction having the composition of methylnaphthalene (Annalen, 1881, 206, 376), and A. Emmert and F. Reingruber soon afterwards showed dimethylnaphthalene to be present (*ibid.* 1882, 211, 365). Schulze (Ber. 1884, 17, 842) seems to have been the first to separate approximately pure  $\alpha$ - and  $\beta$ -methylnaphthalenes, taking advantage of the fact that the  $\beta$ -compound, having a higher melting-point than the  $\alpha$ -, can be frozen out in a fairly pure state from mixtures containing it. Later, Wichelhaus used this method on a coal-tar fraction, b.p. 232–262°, and effected final purification through crystallisation of the picrates, by which means he claimed to have eliminated diphenyl from the methylnaphthalenes (*ibid.* 1891, 24, 3918). Yet both Schulze and Wichelhaus gave the melting-point of the  $\alpha$ -picrate as 116–117° instead of 141°, from which it must be concluded that their  $\alpha$ - contained much  $\beta$ -methylnaphthalene, the picrate of which they eventually isolated from their  $\alpha$ -methylnaphthalene. The true melting-point of the picrate of  $\alpha$ -methylnaphthalene was given at about the same time by R. Meyer and H. Fricko (*ibid.* 1914, 47, 2770) who obtained both  $\alpha$ - and  $\beta$ -methylnaphthalene from the tar formed by polymerising acetylene, and by Lesser (Annalen, 1914, 402, 1) who made the first considerable study of derivatives of both isomers after they had been made commercially available by the German firm, Gesell. f. Teerverwertung m.b.H., Duisberg Meiderich.

G. T. Morgan and E. A. Coulson found both  $\alpha$ - and  $\beta$ -methylnaphthalene in the picrate-forming oil from Kinnell low-temperature coal tar. They encountered the difficulty of separ-

ating pure  $\alpha$ -methylnaphthalene, due to its own low melting-point and to its forming a eutectic with  $\beta$ -methylnaphthalene containing 19% of the latter, having m.p.  $-45$  to  $-44^\circ$ . They obtained pure  $\alpha$ -methylnaphthalene as follows. After freezing out as much  $\beta$ -isomer as possible, the mixed methylnaphthalenes were sulphonated with about twice their weight of concentrated sulphuric acid below  $40^\circ$ . The mixed sulphonic acids were then crystallised from 50% sulphuric acid, in which the  $\alpha$ -methylnaphthalene-4-sulphonic acid is much less soluble than the  $\beta$ -methylnaphthalene-6- and -8-sulphonic acids. After two crystallisations the former is obtained pure; the sulphonic group is removed by hydrolysing with steam in 70% sulphuric acid at  $150^\circ$ , giving pure  $\alpha$ -methylnaphthalene (J.S.C.I. 1934, 53, 73r). E. A. Coulson has also described the isolation of  $\beta$ -methylnaphthalene from a fraction of neutral oil, b.p.  $236$ – $244^\circ$ , from high-temperature tar obtained from horizontal gas retorts. The method used was as follows. The fraction was distilled, the portion having b.p.  $235$ – $245^\circ$  was washed with 60% sulphuric acid, neutralised, dried, and again fractionally distilled. The portion of b.p.  $232$ – $243^\circ$  was subjected to a process of fractional crystallisation at successively higher temperatures, starting at  $-18^\circ$ , until eventually a product of m.p.  $30$ – $33^\circ$ , 98%  $\beta$ -methylnaphthalene, was obtained (*ibid.* 1941, 60, 123).

In a later paper, Coulson obtains  $\alpha$ -methylnaphthalene of high purity from a fraction rich in the  $\alpha$ -isomer (77%  $\alpha$ ) by sulphonating in the cold and diluting the mixture to give 34% sulphuric acid; on cooling, nearly pure  $\alpha$ -methylnaphthalene-4-sulphonic acid separates, and is further purified by two recrystallisations from 34% sulphuric acid. By hydrolysis with dilute sulphuric acid it gives  $\alpha$ -methylnaphthalene of 98–33% purity (*ibid.* 1943, 62, 177). A partial separation of  $\alpha$ - and  $\beta$ -methylnaphthalenes can be effected by sulphonating cold in presence of silver sulphate (giving only sulphonic acids with  $\alpha$ -sulpho-groups) and desulphonating first with sulphuric acid boiling below  $124^\circ$  to obtain a product consisting mainly of  $\alpha$ -methylnaphthalene; when the ratio of hydrolysis slackens, the concentration of sulphuric acid is raised until the temperature reaches  $140$ – $150^\circ$ , when the  $\beta$ -methylnaphthalenesulphonic acids are hydrolysed freely, giving a product rich in  $\beta$ -methylnaphthalene (Coulson, *l.c.*; B.P. 555981).

Mair and Streiff (*see* Table I) have separated both  $\alpha$ - and  $\beta$ -methylnaphthalene from a petroleum kerosene fraction, using an efficient fractionating column. Their constants for the eutectic agree closely with those given by Morgan and Coulson; they give b.p.  $148.3/56$  mm.; m.p.  $-47^\circ$ ; composition, 82.5%  $\alpha$ , 17.5%  $\beta$ .

Both  $\alpha$ - and  $\beta$ -methylnaphthalenes have also been found in Borneo petroleum (H. O. Jones and H. A. Wootton, J.C.S. 1907, 91, 1146) and in Rumanian oil (T. Cosciug, Petroleum, 1935, 31, No. 41, 5; 1938, 34, No. 16, 3). G. T. Morgan reported  $\beta$ -methylnaphthalene in tar from Dalton Main coal carbonised at  $450^\circ$  (Fuel, 1931, 10, 183). Cosciug failed to separate the  $\alpha$ - and  $\beta$ -methylnaphthalene by fractional crystallisation of the picrates (*l.c.*, 1938).

TABLE I.—METHYLNAPHTHALENES.

Orienta- tion.	B.p.	M.p.	Density.	Picrate, m.p.	Source.	Reference.
1-Methyl.				141–142°	Acetylene tar.	Meyer and Fricke, Ber. 1914, 47, 2770.
				141–142°	Coal tar (Ges. für Teerverwertung).	R. Lesser, Annalen, 1914, 402, 1.
	110°/12 mm.			141°	Reduction of $C_{10}H_7 \cdot CH_2Cl$ .	I.G., G.P. 509149, 1930.
	244–78°/760 mm.	–30–77° $\pm 0.06^\circ$	$\rho^{25} 1.0163$ $\pm 0.0001$		Petroleum kerosene fraction.	Mair and Streiff, J. Res. Nat. Bur. Stand. 1940, 24, 395.
2-Methyl.				115°		Schulze, Ber. 1884, 17, 842.
		37–38°		115°	Synthesis.	Fittig and Liebmann, <i>ibid.</i> 1887, 20, 3182.
	240–241°	37–38°		115°	Coal-tar distillate.	Wichelhaus, <i>ibid.</i> 1891, 24, 3918.
		32–33° 34–44		115–116°	As for $\alpha$ -methyl.	R. Lesser, <i>l.c.</i>
	241–14°/760 mm.	$\pm 0.02^\circ$	$\rho^{40} 0.99045$ $\pm 0.00005$		Petroleum kerosene.	Mair and Streiff, <i>l.c.</i>

According to F. Mayer and R. Schiffner (Ber. 1934, 67 [B], 67)  $\alpha$ -methyl and  $\alpha$ -ethyl-naphthalene are each converted into the  $\beta$ -isomers when passed over silica gel at 420–430°.

$\alpha$ -Methylnaphthalene has been found to be a good dispersing medium for use in the hydrogenation of coal (C. H. Fisher and A. Eisner, Ind. Eng. Chem. 1937, 29, 939).

**Synthesis.**— $\alpha$ - and  $\beta$ -Methylnaphthalenes have been synthesised by several methods. R. Fittig and J. Remsen (Annalen, 1870, 155, 114) prepared the  $\alpha$ -compound from  $\alpha$ -bromonaphthalene, methyl iodide, and sodium before it had been isolated from any other source. A better method is to condense naphthalene with formaldehyde and hydrochloric acid to form  $\alpha$ -chloromethylnaphthalene, m.p. 31–32° (I.G., B.P. 337289) and to reduce this with zinc dust, alcohol, and ammonium chloride (I.G., G.P. 509149), or with magnesium (Grummitt and Buck, J. Amer. Chem. Soc. 1943, 65, 295).

$\beta$ -Methylnaphthalene was first synthesised by Fittig and Liebmann (Ber. 1887, 20, 3182). They condensed benzaldehyde with methylsuccinic acid, thereby obtaining two lactic acids which on dry distillation gave two isomeric hydroxy- $\beta$ -methylnaphthalenes, m.p. 89° and 92°, each of which on distillation with zinc dust gave the same  $\beta$ -methylnaphthalene, m.p. 37–38°. This melting-point agrees with that given by Wichelhaus (*l.c.*) but modern observers give a lower value (*see* Table I).

$\beta$ -Methylnaphthalene is a valuable commercially in the United States, the m.p. being 32–5°, purity 98.5% (R. N. Shreve and J. H. Lux, Ind. Eng. Chem. 1943, 35, 306).

## HIGHER ALKYLATED NAPHTHALENES.

Of the ten possible dimethylnaphthalenes, seven have been shown to occur in coal tar, namely the 1:2-, 1:5-, 1:6-, 1:7-, 2:3-, 2:6-, and 2:7-isomers (O. Kruber, Angew. Chem. 1940, 53, 70). The presence of dimethylnaphthalenes in the coal-tar fraction, b.p. 260–265°, was first shown by Emmert and Reingruber (Annalen, 1882, 211, 365), but a practical method of isolating individual hydrocarbons was first pub-

lished by R. Weissgerber and O. Kruber (Ber. 1919, 52 [B], 346; *cf.* Ges. für Teerverwertung, G.P. 301079). By selecting suitable sulphonating conditions, the sulphonic acids of the 1:5-, 2:6-, and 2:7-isomers were obtained pure (*see infra*) and from them the hydrocarbons were recovered by hydrolysis. Later, by similar processes and by fractional crystallisation of the picrates, the other isomers mentioned above were isolated (O. Kruber, *l.c.*; Ber. 1929, 62 [B], 3044), and also  $\beta$ -ethylnaphthalenes. The dimethyl- and ethyl-naphthalenes are stated to constitute about 1–1.2% of the total tar. In the coal-tar fraction boiling at 280–290°, trimethylnaphthalenes have been found, accompanying acenaphthene, fluorene, and diphenyleneoxide; 2:3:6-, 1:3:7-, and 2:3:5-trimethylnaphthalenes were isolated. The trimethylnaphthalenes constitute about 0.1% of the coal tar (O. Kruber, *ibid.* 1939, 72 [B], 1972; 1940, 73 [B], 1174). Although most of these alkyl-naphthalenes are solid at the ordinary temperature, the higher boiling coal-tar fraction is kept fluid because of the large depression of the freezing-point mutually exerted by the ingredients.

T. Cosciug has shown the presence of di- and tri-methylnaphthalenes in Rumanian crude oil, and succeeded in isolating the 2:6 and 2:3:6 derivatives (Petroleum, 1938, 34, No. 17, 4; No. 20, 1). R. Meyer and H. Fricke claim to have isolated 1:4-dimethylnaphthalene from their synthetic acetylene tar (Ber. 1914, 47, 2770).

All the ten possible di- and the fourteen possible tri-methylnaphthalenes are known; they have been synthesised in the course of academic researches, more particularly in connection with the identification of the alkylated naphthalenes obtained by the dehydration and dehydrogenation of naturally occurring vegetable products. They are listed, together with higher homologous alkylated naphthalenes, in the Tables II and III. The synthetic methods used in the preparation of the alkylated naphthalenes are very varied in detail, but they generally consist in fusing a second ring on to a benzenoid compound which may already carry one or more

TABLE II.—DIMETHYLNAPHTHALENES.

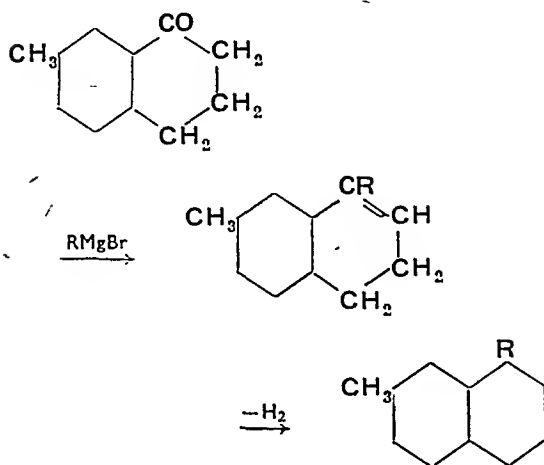
Orientation.	B.p.	M.p.	(a) Picrate, (b) Styphnate, m.p.	Source.	Reference.
1:2-Dimethyl.	139-140°/15 mm. 265°/770 mm.	—3.5°  Liquid.	(a) 129.5-130.5°  (a) 130°  (a) 130-131° (b) 141-143°	Synthesis.  From 1-chloro- methyl-2-methyl.  Coal tar.	Schroeter, Liehtunstadt and Irineu, Ber. 1918, 51, 1587. Darzens and Levy, Compt. rend. 1936, 202, 73. O. Kruber, Angew. Chem. 1940, 53, 70. M. C. Kloetzel, J. Amer. Chem. Soc. 1940, 62, 1708.
1:3-Dimethyl.	107°/1 mm.  126-142°/10 mm.		(a) 118°  (a) 117-118° (b) 116-118° (a) 116-117° (b) 132-133°	Synthesis.  Synthesis.	Barnett and Sanders, J.C.S. 1933, 434. Kloetzel, <i>l.c.</i>  Jitkow and Bogert, J. Amer. Chem. Soc. 1941, 63, 1984.
1:4-Dimethyl.	  118°/10 mm.  264°/760 mm.	  5.5-6.5° (corr.)	(a) 141°  (a) 143-144°  (a) 144° (a) 143-144° (b) 125°	Acetylene tar.  4-Bromo-1-methyl by Grignard and Me <sub>2</sub> SO <sub>4</sub> From 1-methyl-4- chloromethyl.  Synthesis, succinic acid method. Synthesis.	R. Meyer and H. Frieke, <i>ibid.</i> 1914, 47, 2770. Roblison and Thomp- son, J.C.S. 1932, 2015. Darzens and Levy, Compt. rend. 1936, 202, 73. E. de B. Barnett and F. G. Sanders, <i>l.c.</i> M. C. Kloetzel, J. Amer. Chem. Soc. 1940, 62, 1708.
1:5-Dimethyl.		77-78°  82° 80°	(a) 137-138°  (a) 137°	5-Bromo-1-methyl, Mg, Me <sub>2</sub> SO <sub>4</sub> .  Coal tar. From 5-methyl- $\alpha$ - tetralone.	Vesely and Stursa, Coll. Czech. Chem. Comm. 1931, 3, 430. O. Kruber, <i>l.c.</i> Butz, J. Amer. Chem. Soc. 1940, 62, 2557.
1:6-Dimethyl.	265°  262-263°  262-263°		(a) 114°  (a) 114°  (a) 113°	Coal tar.  Coal tar.  Synthesis.	G.P. 301070, Ges. für Teerverwertung (1917). Weissgerber and Krü- ber, Ber. 1919, 52 [B], 346. F. B. Kipping and F. Wild, J.C.S. 1910, 1239.
1:7-Dimethyl.	147-149°/15 mm.  258°/760 mm.  261-262°/760 mm.	Liquid.  84-85°  Liquid.	(a) 123-124°  (a) 114-117°  (a) 120° (a) 121°	Coal tar.  Synthesis.  Synthesis.  Coal tar.	O. Kruber, <i>l.c.</i> Darzens and Heinz, Compt. rend. 1927, 184, 33. Vesely and Medvedeva, Coll. Czech. Chem. Comm. 1931, 3, 440. Barnett and Sanders, <i>l.c.</i> Kruber and Schade, Ber. 1936, 69 [B], 1722.
1:8-Dimethyl.		Liquid. 63°	(a) 141-142° (a) 148° (b) 160°	Coal tar.  Synthesis.	O. Kruber, <i>l.c.</i> Vesely and Stursa, <i>l.c.</i> Linstead <i>et al.</i> , J.C.S. 1937, 1155.
2:3-Dimethyl (guaiane).	139-140°/15 mm. 265-266°/767 mm.	104-105°  104°  105°		Coal tar.  Coal tar.  Synthesis.	Weissgerber, 1919, 52 [B], 370. O. Kruber, <i>ibid.</i> 1929, 62 [B], 3044. Barnett and Sanders, <i>l.c.</i>
2:6-Dimethyl.		110°  100-110°  110°	(a) 123° * (a) 142-143°	Coal tar.  Bromination pro- duct of lonone. Coal tar.	O. Kruber, <i>l.c.</i> , 1940. Bayer and Villiger, Ber. 1899, 32, 2429. Ges. für Teerverwer- tung, G.P. 301070. O. Kruber, <i>l.c.</i> , 1940.
2:7-Dimethyl.	262°/758 mm.	96-97°  97°  97°	(a) 135-136°  (a) 135-136°  (b) 157°  (a) 133-134°	Coal tar.    Dehydrogenation of triterpenes.  2:2:7-Trimethyl- tetralin. Coal tar.	Ges. für Teerverwer- tung, G.P. 301070. Weissgerber and Krü- ber, Ber. 1919, 52 [B], 346. Ruzicka <i>et al.</i> , Helv. Chim. Acta, 1932, 15, 431. Sengupta, J. pr. Chem. 1938, [II], 151, 82. O. Kruber, <i>l.c.</i> , 1940.

\* W. Thiele and G. Trautmann, Ber. 1935, 68 [B], 2245. Garät and Irimescu, Ber. 1941, 74 [B], 1812, give m.p. 130°.

TABLE III.—TRIMETHYLNAPHTHALENES.

Orientation.	B.p.	M.p.	(a) Picrate, (b) Styphnate, m.p.	Source.	Reference.
1:2:3	125–130°/12 mm.		(a) 142·5° (b) 145·5°	Synthesis.	L. Ruzicka and L. Ehmman, <i>Helv. Chim. Acta</i> , 1932, 15, 140.
1:2:4	146°/12 mm. 125–126°/0·6 mm.	54–55° 49–50°	(a) 147·5° (b) 123·5° (a) 148–148·5° (b) 123–124° (a) 146–147°	Synthesis. Synthesis. From 1:4-dimethyl.	<i>Idem, ibid.</i> M. C. Kloetzel, <i>J. Amer. Chem. Soc.</i> 1940, 62, 1708, 3410. C. L. Hewett, <i>J.C.S.</i> 1940, 299.
1:2:5 (agathalene).	147–148°/11 mm.	33·5°	(a) 137–138° (b) 131° (a) 139–140°	Synthesis. Dehydrogenation of tetracyclosqua- lene.	Ruzicka <i>et al.</i> , <i>Helv. Chim. Acta</i> , 1930, 13, 1411. Heilbron and Wilkin- son, <i>J.C.S.</i> 1930, 2546.
1:2:6	146°/10 mm.		(a) 122–123° (a) 120–121° (b) 148°	From bromination product of ionone. Synthesis.	Baeyer and Villiger, <i>Ber.</i> 1899, 32, 2429. Ruzicka and Ehmman, <i>l.c.</i>
1:2:7 (sapotalin).	143°/13 mm.		(a) 129° (b) 156° (a) 130·5–131·5° (b) 159·5–160°	Dehydrogenation of sapogenin and other compounds of triterpene type. Synthesis.	Ruzicka <i>et al.</i> , <i>Helv. Chim. Acta</i> , 1932, 15, 431. Ruzicka and Ehmman, <i>l.c.</i> E. Späth and O. Hromatka, <i>Monatsh.</i> 1932, 60, 117.
1:2:8	152–155°/14 mm.		(a) 133° (b) 144·5°	Synthesis.	Ruzicka and Ehmman, <i>l.c.</i>
1:3:5	143–145°/18 mm. 139·5°/10 mm.	47° 43°	(a) 141–142° (b) 138° (a) 140° (b) 136·5°	Synthesis. Synthesis.	Heilbron and Wilkin- son, <i>J.C.S.</i> 1930, 2537. Ruzicka and Ehmman, <i>l.c.</i>
1:3:6	140–144°/10 mm.		(a) 115° (b) 148°	Synthesis.	Ruzicka and Ehmman, <i>l.c.</i>
1:3:7	131–133°/9 mm.	13·5°	(a) 142° (b) 151·5°	Synthesis. Coal-tar heavy oil.	Ruzicka and Ehmman, <i>l.c.</i> O. Kruber, <i>Ber.</i> 1939, 72 [B], 1972.
1:3:8		48°	(a) 125° (b) 140·5°	Synthesis.	Heilbron and Wilkin- son, <i>l.c.</i>
1:4:5	145°/12 mm.	63° 63°	(a) 144–145° (b) 129–130° (a) 146° (b) 146°	Synthesis.	Ruzicka and Ehmman, <i>l.c.</i> E. de B. Barnett and F. G. Sanders, <i>J.C.S.</i> 1933, 434.
1:4:6	140–142°/15 mm.		(a) 133° (b) 114	Synthesis.	Ruzicka and Ehmman, <i>l.c.</i>
1:6:7 (=2:3:5)	138°/12 mm. 140°/12 mm.	28°	(a) 122° (b) 148–149° (a) 122·5° (b) 146° (a) 125° (b) 149° (a) 125–126° (b) 147·5–148·5°	Synthesis. Synthesis. Synthesis. Synthesis.	Wilkinson, <i>J.C.S.</i> 1931, 1333. Ruzicka and Ehmman, <i>l.c.</i> Barnett and Sanders, <i>l.c.</i> Pope and Bogert, <i>J.</i> <i>Org. Chem.</i> 1938, 2, 276.
2:3:6	146–148°/14 mm. 286°/762 mm.	102°	(a) 130° (b) 165° (a) 130°	Synthesis. Coal-tar heavy oil.	Ruzicka and Ehmman, <i>l.c.</i> O. Kruber, <i>Ber.</i> 1939, 72 [B], 1972; <i>Angew.</i> <i>Chem.</i> 1940, 53, 70.

alkyl substituents. For instance *p*-tolylbutyric acid may be cyclised to give 7-methyl-1-keto-1:2:3:4-tetrahydronaphthalene, whence 2-methylnaphthalene can be obtained or, by a Grignard reaction followed by dehydration and dehydrogenation, a 1-alkyl-7-methylnaphthalene:



Examples of synthesis will be given under specific compounds.

Dialkylnaphthalenes of the 1:4-series can be obtained according to Scott, Walker, and the Du Pont Co., by the reaction of the 1:4-disodium addition compound of naphthalene with an alkyl halide in ether, and dehydrogenation of the dialkyl-1:4-dihydronaphthalene so obtained (U.S.P. 2150039).

Ethyl and higher alkyl groups can be introduced into the naphthalene nucleus by several methods not available for introducing methyl groups. Acylnaphthalenes, *e.g.*, acetylnaphthalenes, by reduction give the corresponding alkylnaphthalenes. Olefins such as ethylene, propylene, and isobutylene condense with naphthalene under the influence of a variety of catalysts to give alkylnaphthalenes. Alcohols such as isopropyl and isobutyl alcohols condense with naphthalene in concentrated sulphuric acid giving mixtures of mono- and higher alkylated naphthalenesulphonic acids which have important industrial applications as wetting agents. Other methods of preparing secondary alkylnaphthalenes depend on the application of the Grignard reaction to esters of naphthoic acids and to naphthyl alkyl ketones.

Alkyl halides can be condensed with naphthalene in presence of aluminium chloride, and alcohols in presence of boron trifluoride.

## DERIVATIVES OF $\alpha$ -METHYLNAPHTHALENE.

### Halogeno Derivatives.

1-Chloromethylnaphthalene is formed when hydrogen chloride is led into a mixture of naphthalene, aqueous formaldehyde, and hydrochloric acid at 60–65° for ten hours. The oil which separates gives on distillation 1-chloromethylnaphthalene, b.p. 153°/12 mm.; m.p. 31–32° (I.G., B.P. 337289). In a similar manner

5-nitro-1-chloromethylnaphthalene, m.p. 96–97°, is obtained from 1-nitronaphthalene (I.G., B.P. 473522); further chlorination of the product by means of chlorine in the presence of an antimony halide and a solvent gives 4-chloro-5-nitro-1-chloromethylnaphthalene, m.p. 130–131° (I.G., B.P. 529587). The nitration of 1-chloromethylnaphthalene (8-nitro derivative, m.p. 105°) is described by V. A. Ismailski and A. N. Kozin (Compt. rend. Acad. Sci. U.R.S.S. 1940, 28, 621).

J. S. H. Davies and A. E. Oxford (J.C.S. 1931, 221) chlorinated 1-methylnaphthalene and from the product obtained 1-chloromethylnaphthalene in silvery flakes, m.p. 29.5–30.5°. The preparation and reactions of 1-naphthylmethylmagnesium chloride have been studied by H. Gilman and J. E. Kirby (J. Amer. Chem. Soc. 1929, 51, 3475).

The action of bromine on 1-methylnaphthalene in sunlight at 230° gives 1-bromomethylnaphthalene, m.p. 45–46° (W. Wislicenus and H. Elvert, Ber. 1916, 49, 2822; *cf.* F. Mayer and A. Sieglitz, *ibid.* 1922, 55 [B], 1835). Olivier and Wit (Rec. trav. chim. 1937, 56, 856) give m.p. 53° for the pure compound, whilst F. E. King and T. Henshall (J.C.S. 1945, 417) give m.p. 55°. J. von Braun and K. Moldaenke (Ber. 1923, 56 [B], 2165) obtained the compound by the action of phosphorus pentabromide on benz- $\alpha$ -naphthylmethylamide, m.p. 154°. It is highly lachrymatory.

5-Methoxy- $\alpha$ -naphthylmethylbromide has m.p. 98° (Shoosmith and Rubli, J.C.S. 1927, 3104).

Nuclear chlorination of  $\alpha$ -methylnaphthalene is brought about by heating with sulphuryl chloride at 35–40°, when 4-chloro-1-methylnaphthalene, b.p. 278–283°, is obtained (I.G., B.P. 263844). 2-Chloro-1-methylnaphthalene was prepared by R. Scholl, C. Seer, and A. Zinke (Monatsh. 1920, 41, 589) from the 2-amino-compound; it has b.p. 144–145°/12 mm., and on nitration gives two nitro derivatives, m.p. 133–134° and 70–80° respectively.

8-Chloro-1-methylnaphthalene was obtained by L. F. Fieser and A. M. Seligman (J. Amer. Chem. Soc. 1939, 61, 136) from 1:8-chlorobromonaphthalene by the action of its magnesium compound with dimethyl sulphate. It has m.p. 68–69°, *picrate*, m.p. 138.5–139.5°. In the same way from 1:8-bromoiodonaphthalene they prepared 8-bromo-1-methylnaphthalene.

By exhaustively chlorinating  $\alpha$ -methylnaphthalene in the cold and boiling the product with alcoholic potassium hydroxide, O. Schorler (Ber. 1891, 24, 3927) obtained a trichloro- $\alpha$ -methylnaphthalene, m.p. 145–6°.

4-Bromo-1-methylnaphthalene is obtained by brominating 1-methylnaphthalene in the dark in carbon disulphide (F. Meyer and A. Sieglitz, *ibid.* 1922, 55 [B], 1835) or carbon tetrachloride (R. Robinson and H. W. Thompson, J.C.S. 1932, 2016). The latter authors obtained the compound crystalline, m.p. 5.5–6.0° (corr.), b.p. 157–158°/10 mm., *picrate*, m.p. 126–127°. L. F. Fieser and A. M. Seligman (J. Amer. Chem. Soc. 1939, 61, 136) say that a better preparative method is to brominate potassium 1-methylnaphthalene-4-sulphonate in aqueous solution, when the sulphonic group is displaced by

bromine. They give m.p. 7°, *picrate*, m.p. 128–129°.

The following bromo-1-methylnaphthalenes were prepared by V. Veselý, F. Štursa, H. Olejníček, and E. Rein (Coll. Czech. Chem. Comm. 1930, 2, 145) by the diazo-reaction from amino-compounds:

2-bromo-1-methylnaphthalene, m.p. 35–36°; *picrate*, m.p. 105–106°.

3-bromo-1-methylnaphthalene, m.p. 46–47°; *picrate*, m.p. 83–84°.

5-bromo-1-methylnaphthalene, m.p. 63–64°; *picrate*, m.p. 110–111°.

8-bromo-1-methylnaphthalene, m.p. 80°; *picrate*, m.p. 152–153°.

2:4-dibromo-1-methylnaphthalene, m.p. 58–59°.

7-Bromo-1-methylnaphthalene, b.p. 124–125/3 mm. (*picrate*, m.p. 92.5–93.5°) was synthesised by L. P. Fieser and A. M. Seligman (J. Amer. Chem. Soc. 1938, 60, 170) from *p*-bromophenylbutyryl chloride through 7-bromotetralone, m.p. 76–77°.

2-Iodo-1-methylnaphthalene, m.p. 51.5°, was prepared by Scholl and Tritsch (Monatsh. 1918, 39, 233) from the 2-amino-compound. When heated with copper powder at 220–260° it gives 1:1'-dimethyl-2:2'-dinaphthyl, m.p. 230° (cf. Mayer and Schnecko, Ber. 1923, 56 [B], 1408).

### Nitro Derivatives.

The nitration of 1-methylnaphthalene has been studied by R. Lesser (Annalen, 1914, 402, 1) (who was the first to examine systematically the substitution products of 1- and 2-methylnaphthalenes), by V. Veselý, F. Štursa, H. Olejníček, and E. Rein (Coll. Czech. Chem. Comm. 1929, 1, 493) and by H. W. Thompson (J.C.S. 1932, 2310). According to Thompson, nitration in acetic acid, acetic anhydride or nitromethane with pure nitric acid at 0° or with nitric acid,  $\rho$  1.42, at 15° all give the same result. Nitration takes place readily and the temperature must be controlled. The main product, about 70% (Thompson) is 4-nitro-1-methylnaphthalene, m.p. 68–69° (Veselý *et al.*), with some 5-nitro-, less 2-nitro-, and, according to Veselý, a trace of 8-nitro-1-methylnaphthalene. According to Lesser, oxidation of 4-nitro-1-methylnaphthalene with permanganate gives no trace of an acid, but a small yield of 4-nitro-1-naphthoic acid can be obtained by heating it with 8% nitric acid for 12 hours at 135–140°.

Further nitration of 4-nitro-1-methylnaphthalene gives 45% of 4:5-dinitro-1-methylnaphthalene, m.p. 143° (Thompson, *l.c.*; Veselý *et al.*, Coll. Czech. Chem. Comm. 1930, 2, 145), some 2:4-dinitro-1-methylnaphthalene, m.p. 160–161° (Veselý *et al.*), a small amount of 4:8-dinitro-, m.p. 122–123° (Thompson), and a trace of a dinitro-1-methylnaphthalene, m.p. 176°. By nitrating 2:4- or 4:5-dinitro-1-methylnaphthalene, Thompson obtained 2:4:5-trinitro-1-methylnaphthalene, pale yellow prisms, m.p. 170°. Characteristic colours are given when, to a solution of 2:4-dinitro- or 2:4:5-trinitro-1-methylnaphthalene in alcohol or acetone, caustic soda or ammonia is added.

2:4-Dinitro-1-methylnaphthalene is formed when 2:4-dinitro-1-naphthylacetic acid is melted

or treated with cold pyridine (V. Veselý and I. Pastak, Bull. Soc. chim. 1925, [iv], 37, 1444). The methyl group is reactive towards aromatic aldehydes and *p*-nitrosodimethylaniline.

When 4-nitro-1-methylnaphthalene is brominated in ultra-violet light bromination takes place only in the nucleus, giving a monobromo-4-nitro-1-methylnaphthalene, m.p. 137.5–138.5°, and a tetrabromo-4-nitro-1-methylnaphthalene, m.p. 189–190° (decomp.) (Davies and Oxford, J.C.S. 1931, 221).

The isomeric mononitro-1-methylnaphthalenes have all been described by Veselý *et al.* (*l.c.* 1929).

2-Nitro-1-methylnaphthalene, m.p. 58–59°, was obtained from 2-nitro-4-amino-1-methylnaphthalene.

3-Nitro-1-methylnaphthalene, m.p. 81–82°, from 3-nitro-4-amino-1-methylnaphthalene.

5-Nitro-1-methylnaphthalene, m.p. 82–83°, from 5-nitro-1-methylnaphthalene-4-sulphonic acid.

6-Nitro-1-methylnaphthalene, m.p. 76–77°, from 6-nitro-5-amino-1-methylnaphthalene.

7-Nitro-1-methylnaphthalene, m.p. 98–99°, from 7-nitro-8-amino-1-methylnaphthalene.

8-Nitro-1-methylnaphthalene, m.p. 63–64°, from its 4-sulphinic acid.

According to R. E. Steiger (Helv. Chim. Acta, 1933, 16, 793) 8-nitro-1-methylnaphthalene, m.p. 65° (corr.), and its 5-sulphonamide, m.p. 236°, are both highly sensitive to light; he attributes this to the close proximity of the nitro and methyl groups.

### Sulphonic Acids.

When 1-methylnaphthalene is sulphonated with sulphuric acid at the ordinary temperature (K. Elbs and B. Christ, J. pr. Chem. 1923, [ii], 106, 17) or with chlorosulphonic acid in carbon tetrachloride at 0° (R. E. Steiger, Helv. Chim. Acta, 1930, 13, 173) the principal product is the 4-sulphonic acid (73% by Steiger's method), and a small amount of an isomer shown by Veselý and Štursa (Coll. Czech. Chem. Comm. 1931, 3, 328) to be the 5-sulphonic acid. At high temperatures sulphonation, as in the case of naphthalene, gives  $\beta$ -sulphonic acids. Fieser and Bowen (J. Amer. Chem. Soc. 1940, 62, 2105) prefer the chlorosulphonic acid method for preparing the 4-sulphonic acid.

1-Methylnaphthalene-4-sulphonic acid forms a barium salt,  $1\text{H}_2\text{O}$ , and copper salt,  $4\text{H}_2\text{O}$ ; sulphochloride, m.p. 81°; sulphonamide, m.p. 174°; sulphonanilide, m.p. 158°; methyl ester, m.p. 107°; ethyl ester, m.p. 98° (Elbs and Christ, *l.c.*). By nitration of the sulphochloride a mixture of the 5- and 8-nitro derivatives is obtained (Steiger, Helv. Chim. Acta. 1934, 17, 1142, 1354). 5-Nitro-1-methylnaphthalene-4-sulphonyl chloride decomposes at 170°, the amide has m.p. 228°, and anilide, m.p. 256° (decomp.). The derivatives of this nitro-acid are all very sensitive to light.

Reduction of 1-methylnaphthalene-4-sulphonyl chloride with zinc dust gives the 4-sulphinic acid, needles, m.p. 114–115°, which forms a sodium salt,  $3\text{H}_2\text{O}$ ; reduction with iron and hydrochloric acid gives the 4-thiol (Elbs and Christ, *l.c.*). 1-Methylnaphthalene-5-sulphonic

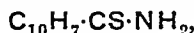


acid forms a *sulphonamide*, m.p. 176–178° (Vesely, *l.c.*).

Sulphonation of 1-methylnaphthalene at higher temperatures gives mainly the 3- and 6-sulphonic acids. The 6-sulphonic acid was isolated as its barium salt by K. Dziewoński and T. Waszkowski (Bull. Acad. Polonaise, 1929, A, 604) who at first considered it to be the 7-sulphonic acid but later the error was corrected by Dziewoński and M. Otto (*ibid.* 1935, A, 201). It was obtained by sulphonating with sulphuric acid ( $\rho$  1.84) at 150–170°; 1-methylnaphthalene-6-sulphonyl chloride has m.p. 120–122°; *sulphonamide*, m.p. 188–189°. Using ordinary concentrated sulphuric acid at 110–120°, Vesely and Štursa (Coll. Czech. Chem. Comm. 1931, 3, 328) isolated, as the barium salt, 1-methylnaphthalene-3-sulphonic acid, characterised by the chloride, m.p. 124–125°, and *amide*, m.p. 143–144°. Later Dziewoński and E. Kowalczyk (Bull. Acad. Polonaise, 1935, A, 559) stated that sulphonation with 100% sulphuric acid at 165–175° gives a mixture of 3-, 6-, and 7-sulphonic acids, the first two being separated through the different solubilities of their barium salts in water, whilst the barium salt of the last is soluble in alcohol. They give for 1-methylnaphthalene-7-sulphonyl chloride, m.p. 88°, *sulphonamide*, m.p. 116°, but I.G., who prepared the 7-sulphonic acid by eliminating the amino group from 1-methyl-4-naphthylamine-7-sulphonic acid (B.P. 462468), give for the *sulphonyl chloride* m.p. 107° and *sulphonamide* m.p. 131°; *sulphonanilide*, m.p. 149°. The I.G. product was converted by caustic fusion into a naphthol of the same melting-point as the 1-methyl-7-naphthol prepared by an independent route.

#### Amino Derivatives.

$\alpha$  - Naphthylmethylamine,  $C_{10}H_7 \cdot CH_2 \cdot NH_2$ , sometimes called *menaphthylamine*, was first prepared by A. W. Hofmann (Ber. 1868, 1, 101) by reduction of  $\alpha$ -naphth-thioamide,



with zinc and hydrochloric acid. It is a caustic liquid, b.p. 290–293°, forming a readily crystallisable *hydrochloride* and a *platinichloride*. It has also been prepared by heating 1-menaphthyl chloride with hexamethylenetetramine in chloroform (F. F. Blicke, C. E. Maxwell, J. Amer. Chem. Soc. 1939, 61, 1780). It forms a crystalline nitrite, readily decomposed by water to  $\alpha$ -naphthylcarbinol (Bamberger and Lodter, Ber. 1888, 21, 258). For the N-alkyl derivatives of 1-menaphthylamine, see J. von Braun and K. Moldaenke, *ibid.* 1923, 56 [B], 2165.

All the nuclear monoamino derivatives of 1-methylnaphthalene are known, see Table IV, and were obtained by reduction of the corresponding nitro-compound, but the 7-amino-compound was obtained in purer form by aminating the 7-hydroxy-compound. Attempts to methylate naphthylamines in the nucleus have failed (see D. H. Hey and E. R. B. Jackson, J.C.S. 1936, 1783).

Reduction of 2:4-dinitro-1-methylnaphthalene by hydrogen (platinum black) or by ammonium hydrogen sulphide gives 2-nitro-4-amino-1-

TABLE IV.—AMINO DERIVATIVES OF 1- AND 2-METHYLNAPHTHALENES.

Orientat-ion.	M.p.	(a) Acetyl, (b) Benzoyl, m.p.	References.
Me:NH <sub>2</sub> 1:2-	40–50°	(a) 188–189° (b) 222°	Vesely <i>et al.</i> , Coll. Czech. Chem. Comm. 1929, 1, 493.
1:3-	68°	(a) 172–173°	<i>Idem, ibid.</i>
1:4-	51–52°	(a) 166–167° (b) 238–239°	Lesser, Annalen, 1914, 402, 1.
1:5-	77–78°	(a) 194–195° (b) 173–174°	Vesely <i>et al.</i> , <i>l.c.</i>
1:6-	63–64°	(a) 123–124° (b) 155–156°	<i>Idem, ibid.</i>
1:7-	85–86°	(a) 157–158°	Vesely and Štursa, Coll. Czech. Chem. Comm. 1933, 5, 170.
1:8-	67–68°	(a) 183–184° (b) 195–196°	Vesely <i>et al.</i> , <i>ibid.</i> 1929, 1, 493.
2:1-	32°	(a) 188° (b) 180°	Lesser, <i>l.c.</i>
2:4-	51–52°	(a) 175–176°	Vesely and Kapp, Chem. Listy, 1924, 18, 201, 244.
2:5-	90°	(a) 160–161°	Vesely and Pač Coll. Czech. Chem. Comm. 1930, 2, 471.
2:6-	129–130°	(a) 155–156°	Dziewoński, Schoe- nówna, and Wald- mann, Ber. 1925, 58 [B], 1211.
2:7-	105°	(a) 152°	Vesely and Pač, <i>l.c.</i>
2:8-	57–58°	(a) 181–183° (b) 194–195°	<i>Idem, ibid.</i>

methylnaphthalene, m.p. 131–132° (acetyl, m.p. 230–231°), but reduction with stannous chloride yields also 4-nitro-2-amino-1-methylnaphthalene, m.p. 126–128° (acetyl, m.p. 203–204°, Vesely *et al.*, Coll. Czech. Chem. Comm. 1930, 2, 145). 4-Bromo-2-amino-1-methyl- has m.p. 78° (acetyl, m.p. 223–224°) and 2-bromo-4-amino-1-methyl-naphthalene, m.p. 118–119° (acetyl, m.p. 206–207°).

Nitration of 4-acetamido-1-methylnaphthalene with nitric acid ( $\rho$  1.52) in acetic anhydride solution gives 3-nitro-4-acetamido-1-methylnaphthalene, m.p. 224–225°, whence 3-nitro-4-amino-1-methylnaphthalene, m.p. 179–180°, is obtained. Similar nitration of 5-acetamido-1-methylnaphthalene gives a mixture of 6- and 8-nitro derivatives, whence are obtained 6-nitro-5-amino-1-methyl-, m.p. 178–179° (acetyl, m.p. 245–246°) and 8-nitro-5-amino-1-methylnaphthalene, m.p. 163–164° (acetyl, m.p. 197–198°). By nitrating 8-acetamido-1-methylnaphthalene are obtained 5-nitro-8-amino-1-methyl-, m.p. 162–163° (acetyl, m.p. 193–194°), and 7-nitro-8-amino-1-methylnaphthalene, m.p. 150–152° (acetyl, m.p. 186–187°) (Vesely *et al.*, *l.c.* 1929).

Sulphonation of 4-amino-1-methylnaphthalene with 100% sulphuric acid, or a mixture of sulphuric and chlorosulphonic acids at temperatures

from 100° to 160° gives a mixture of 65% of the 2- and 35% of the 7-sulphonic acid (I.G., B.P. 462465).

The following diamino-1-methylnaphthalenes have been described: 3:4-diamino-, m.p. 91° (Lesser, *l.c.*, Veselý *et al.*, *l.c.* 1929), 4:5-diamino-, m.p. 64° (Thompson, *l.c.*), and 5:6-diamino-, m.p. 151–152° (Veselý *et al.*, *l.c.*); 2:4-diamino-, m.p. 93° (Thompson, J.C.S. 1932, 1830); 5:8-diamino- (Veselý *et al.*, *l.c.*). The diacetyl derivative of 2:4-diamino-1-methylnaphthalene, which was obtained by Thompson by a synthetic method as well as from the diamine from the dinitro-compound, has m.p. 303°.

### Hydroxy Derivatives.

$\alpha$ -Naphthylcarbinol, m.p. 59–56°, has been prepared by the action of nitrous acid on  $\alpha$ -naphthylmethylamine (*v.s.*) and also by the action of formaldehyde on  $\alpha$ -naphthyl magnesium bromide (K. Ziegler, Ber. 1921, 54 [B], 737).

The following 1-methylnaphthols have been described.

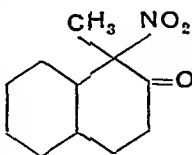
1-Methyl-2-naphthol, obtained by alkali fusion of the 2-sulphonic acid, has m.p. 110° (I.G., B.P. 462465); also by reduction with zinc dust and sodium hydroxide of 2:2'-dihydroxy-1:1'-dinaphthylmethane (Meister, Lucius, and Brüning, G.P. 161450, 1904; m.p. 112°). It forms a methyl ether, m.p. 41–42° (Scholl and Neuberger, Monatsh. 1912, 33, 518), acetyl derivative, m.p. 66°. The latter method was studied by Fries and Hübner (Ber. 1906, 39, 435) and improved by Robinson and Weygand (J.C.S. 1941, 387). Fries and Hübner (*l.c.*) describe 6-bromo-, m.p. 129°, and 3:6-dibromo-1-methyl-2-naphthol, m.p. 180°, and Veselý *et al.* (*l.c.* 1930) 4-bromo-1-methyl-2-naphthol, m.p. 108–109°.

1-Methyl-2-naphthol is also obtained when  $\beta$ -naphthylamine hydrochloride is heated with 4 mol. proportions of methyl alcohol at 240–250° (Hey and Jackson, J.C.S. 1936, 1783).

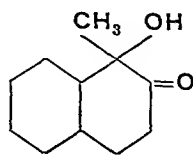
The halogenation of 1-methyl-2-naphthol has been studied. Bromination proceeds normally in acetic acid solution (Fries and Hübner, *l.c.*) but chlorination, as with  $\beta$ -naphthol, pursues a different course, giving first 1-chloro-1-methyl-2-keto-1:2-dihydronaphthalene and then, by addition of chlorine, 1:3:4-trichloro-1-methyl-2-keto-1:2:3:4-tetrahydronaphthalene, m.p. 78°. In the course of this work 3-chloro-, m.p. 60°, and 3:4-dichloro-1-methyl-2-naphthol, m.p. 132°, were prepared (Fries and Hempelmann, Ber. 1908, 41, 2614). 4-Chloro-1-methyl-2-naphthol, m.p. 101°, was obtained by Fries (*ibid.* 1921, 54 [B], 2928) from 1-chloro-1-methyl-2-ketodihydronaphthalene (*cf.* Fries and Engel, Annalen, 1924, 439, 232).

The action of nitrous acid on 1-methyl-2-naphthol presents interesting features. According to conditions there may be obtained 1:2-methylnaphthaquinonitrole, m.p. 60° (I), which when warmed with acetic acid gives 1:2-methylnaphtha- $\psi$ -quinol, m.p. 89° (II); or 1:2-naphthamethylenequinone, m.p. 132° (III) (Fries and Hübner, *l.c.*). The last compound was also obtained, m.p. 133–134°, by Pummerer and Cherbuliez (Ber. 1914, 47, 2957) by oxidising

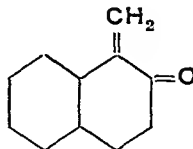
1-methyl-2-naphthol with alkaline ferricyanide or with ferric chloride; on both physical and chemical grounds they rejected formula III for the compound (which they called dehydro-1-



I.

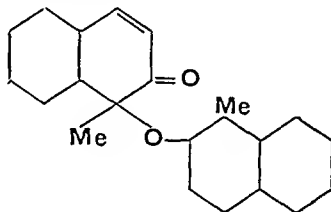


II.



III.

methyl-2-naphthol), and Pummerer later concluded that its most probable structure is (IV) (*ibid.* 1919, 52 [B], 1403).



IV.

1-Methyl-3-naphthol, m.p. 81–82°, was obtained by Veselý *et al.* (*l.c.* 1929) from 1-methyl-3-naphthylamine, and by Veselý and Štursa (Coll. Czech. Chem. Comm. 1931, 3, 328) from the 3-sulphonic acid.

1-Methyl-4-naphthol was described by Lesser (Annalen, 1914, 402, 1) as having a characteristic odour somewhat different from that of  $\alpha$ -naphthol; m.p. 84–85°, benzoyl derivative m.p. 81–82°. It was prepared from 1-methyl-4-naphthylamine. 2-Bromo-1-methyl-4-naphthol has m.p. 128–129° (Veselý *et al.*, *l.c.* 1930).

1-Methyl-5-naphthol, from the amine, has m.p. 97–98° (Veselý *et al.*, *l.c.* 1929; *cf.* Veselý and Štursa, Coll. Czech. Chem. Comm. 1931, 3, 328).

1-Methyl-6-naphthol, from the 6-sulphonic acid (Dziewonski and Otto, Bull. Acad. Polonaise, 1935, A, 201), first described as the 7-naphthol, has m.p. 107–108°.

1-Methyl-7-naphthol, m.p. 69–70°, was obtained by Veselý and Štursa (Coll. Czech. Chem. Comm. 1933, 5, 170), by a synthetic method, via 7-methoxy-1-keto-1:2:3:4-tetrahydronaphthalene, m.p. 67–68°; and by I.G. (B.P. 462468) from 1-methylnaphthalene-7-sulphonic acid. Its methyl ether has m.p. 47–48°.

6:7-Dimethoxy-1-methylnaphthalene, m.p. 110–111° (picrate, m.p. 116–117°) has been made by a synthetic method (Haworth and Mavin J.C.S. 1932, 1485).

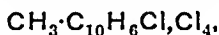
## DERIVATIVES OF $\beta$ -METHYLNAPHTHALENE.

### Halogeno Derivatives.

By passing a stream of chlorine into 2-methylnaphthalene at 240–250°, Schulz (Ber. 1884, 17, 1529) obtained 2-naphthylmethyl chloride ( $\beta$ -menaphthyl chloride), m.p. 47°, b.p. 168°/20 mm. In a similar manner, brominating at 240°, he obtained  $\beta$ -menaphthyl bromide, m.p. 56°, b.p. 213°/100 mm. Both are highly lachrymatory. According to Olivier and Wit (Rec. trav. chim. 1938, 57, 90) the best yield of the bromide, 37%, is obtained by brominating in the light of a Philips "solar light" lamp at 230°, and they claim that the crude bromide can be distilled without appreciable decomposition at 14 mm., whilst the pure compound loses hydrogen bromide forming a polymer ( $C_{11}H_8$ )<sub>n</sub>, the amount of decomposition depending on the kind of glass used, pyrex glass giving least decomposition.

J. B. Shoesmith and A. Mackie (J.C.S. 1930, 1584) prepared 1-chloro-, m.p. 81°, and 3-chloro-2-naphthylmethyl bromide, m.p. 97°, and studied their hydrolysis by aqueous alcohol; the rates were approximately equal.

The chlorination of 2-methylnaphthalene in the cold was studied by Seherler (Ber. 1891, 24, 3921). By prolonged chlorination he obtained a semi-solid product from which was isolated a methylechloronaphthalene tetrachloride,



m.p. 148°, which when boiled with alcoholic potash gave a trichloro-2-methylnaphthalene, m.p. 182°, presumably the 1:3:4-trichloro-compound since it gave phthalic acid on oxidation. Chlorination in the cold in sunlight gave a chloro-2-methylnaphthalene, b.p. 159–161°/25 mm., which formed a picrate, m.p. 106–107°.

When 2-methylnaphthalene was chlorinated in diffused light at 220°, O. Achmatowicz and K. Lindenfeld (Rocz. Chem. 1938, 18, 69) obtained a complex mixture from which they isolated 1-chloro-2-methylnaphthalene, b.p. 162–164°/30 mm., identical with Seherler's compound, 2-naphthylmethyl chloride, 1-chloro-2-chloromethylnaphthalene, m.p. 78–79° and 2-dichloromethylnaphthalene, m.p. 114–115°. 1-Chloro-2-methylnaphthalene is also obtained by the action of sulphuryl chloride on 2-methylnaphthalene (I.G., B.P. 263844).

Bromination of 2-methylnaphthalene in carbon disulphide gives a 70% yield of 1-bromo-2-methylnaphthalene, b.p. 290–295°/760 mm. (picrate, m.p. 113°) (Mayer and Sieglitz, Ber. 1922, 55 [B], 1835). From the corresponding aminomethylnaphthalenes Vesely and Kapp (Chem. Listy, 1924, 18, 201, 244) prepared 4-bromo- (picrate, m.p. 90–91°), 5-bromo- (picrate, m.p. 91–92°) and 8-bromo-2-methylnaphthalene (picrate, m.p. 99–100°).

### Nitro Derivatives.

2-Methylnaphthalene is readily nitrated, the principal mono-nitration product being 1-nitro-2-methylnaphthalene, m.p. 81° (Schulz, l.c., Lesser, l.c., and other authors). According to Vesely and Kapp (Chem. Listy, 1924, 18, 201, 244), three other nitro-compounds are formed at

the same time, namely, the 4-, 6-, and 8-nitro derivatives. When the crude product was reduced by alcoholic ammonium sulphide the 1-nitro-compound remained unattacked, and the amines formed were separated and identified by means of their acetyl or benzoyl derivatives. 4-Nitro-2-methylnaphthalene, m.p. 49–50°, was prepared from 4-nitro-1-amino-2-methylnaphthalene. The following were prepared in a similar manner from nitroamines by Vesely and Páček (Coll. Czech. Chem. Comm. 1930, 2, 471): 5-nitro-, m.p. 61–62°; 6-nitro-, m.p. 119°; 7-nitro-, m.p. 105°; and 8-nitro-2-methylnaphthalene, m.p. 36–38°. Vesely and Kapp (l.c.) prepared 5-bromo-1-nitro-, m.p. 94°, and 1-bromo-4-nitro-2-methylnaphthalene, m.p. 100–101°, and Vesely, Medvedeva, and Müller (ibid. 1935, 7, 228) chlorinated 1-nitro-2-methylnaphthalene in the presence of ferric chloride to obtain 8-chloro-1-nitro-2-methylnaphthalene, m.p. 114°. The methyl group of 1-nitro-2-methylnaphthalene is so reactive that the compound condenses with ethyl oxalate in the presence of potassium ethoxide to form ethyl 1-nitro-2-naphthylpyruvate, and when excess of potassium ethoxide is used, 1:1'-dinitro-2:2'-dinaphthylethane, m.p. 251°, is formed (Wislicenus and Thoma, Annalen, 1924, 436, 62).

By nitrating 2-methylnaphthalene-1-sulphonyl chloride, Vesely and Páček (l.c. 1930) obtained a mixture from which were separated 8-nitro-, m.p. 145°, and 5-nitro-2-methylnaphthalene-1-sulphonyl chloride, m.p. 84–85°. These when reduced to sulphinic acids and hydrolysed with 60% sulphuric acid gave the corresponding nitro-2-methylnaphthalenes.

Dinitration of 2-methylnaphthalene gives at least two products, the 1:8-dinitro, m.p. 209°, and 1:5-dinitro-2-methylnaphthalene, m.p. 134°; they were also obtained by nitrating respectively 8- and 5-nitro-2-methylnaphthalenes (Vesely and Kapp, l.c.; Vesely and Páček, l.c.). 8-Chloro-5:7-dinitro-2-methylnaphthalene has been prepared by Vesely and Medvedova (Coll. Czech. Chem. Comm. 1931, 3, 440).

### Sulphonic Acids.

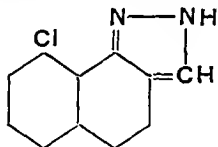
Sulphonation of 2-methylnaphthalene may give the 6-, 7-, or a mixture of the 8- and 1-sulphonic acids according to conditions. Using concentrated sulphuric acid,  $\rho$  1.84, in slight excess at 90–100° for 5–6 hours, Dziewoński, Schoenówna, and Waldmann (Ber. 1925, 58 [B], 1211) obtained an 80% yield of 2-methylnaphthalene-6-sulphonic acid, isolated as the barium salt (sulphonyl chloride, m.p. 97–98°, sulphonamide, m.p. 205–206°, ethyl ester, m.p. 79–80°). By sulphonating with 1 mol. proportion of chlorosulphonic acid in nitrobenzene solution at 30–40°, Dziewoński and Wulfssohn (Bull. Acad. Polonaise, 1929, A, 143) obtained 2-methylnaphthalene-8-sulphonic acid (chloride, m.p. 94–96°, amide, m.p. 172–174° or 195–196°; anilide, m.p. 162–164°), whilst Vesely and Páček, using chlorosulphonic acid at –5° (Coll. Czech. Chem. Comm. 1930, 2, 471) obtained, besides the 8-sulphonic acid, a smaller quantity of 2-methylnaphthalene-1-sulphonic acid; the sulphonyl chloride has m.p. 83–85°, amide, m.p. 124°.

According to Shreve and Lux (Ind. Eng. Chem. 1943, 35, 306), the sulphonic acid obtained by sulphonating with 93% sulphuric acid depends on the temperature. At 40° the product is mainly the 8-sulphonic acid (75% yield), at 90–100° the 6-sulphonic acid (90% yield), and above 160° the 7-sulphonic acid (chloride, m.p. 63–64°; amide, m.p. 163–164°).

### Amino Derivatives.

The properties of the six known amino-2-methylnaphthalenes are included in Table IV; they are usually prepared by reduction of the nitro-compounds with iron and acetic acid though the 6-amino-compound is obtained from 6-hydroxy-2-methylnaphthalene by the action of ammonia and ammonium sulphite at 150°. When the reduction is carried out with tin and hydrochloric acid, however, halogenation may also occur; thus 1-nitro-2-methylnaphthalene under these conditions gives 4-chloro-1-amino-2-methylnaphthalene, m.p. 65° (acetyl derivative, m.p. 206°; benzoyl, m.p. 236–237°) (Lesser, Annalen, 1913, 402, 1). 8-Chloro-1-amino-2-methylnaphthalene (acetyl, m.p. 214–215°) obtained by reduction of the nitro-compound has m.p. 89°. 5-Bromo-1-amino-2-methylnaphthalene has m.p. 53–55°. 1-Amino-2-methylnaphthalene-4-sulphonic acid was prepared by H. E. Fierz-David and E. Mannhart (Helv. Chim. Acta, 1937, 20, 1024) and compared with naphthionic acid as an azo-dye component.

The diazo-compounds from 1-amino-2-methylnaphthalenes show abnormal behaviour, due to internal reaction between the diazo and methyl groups. Thus 8-chloro-1-amino-2-methylnaphthalene gives, when its diazo derivative is boiled with ethyl alcohol, 9-chloro-[a]-naphthindazole, m.p. 159°.



and 4-nitro-1-amino-2-methylnaphthalene is similarly converted into 5-nitro-[a]-naphthindazole, m.p. 304–305°. The nitroso derivative of 1-acetamido-2-methylnaphthalene gives [a]-naphthindazole, m.p. 158°, when cautiously heated (Vesely, Medvedeva, and Müller, *l.c.*).

Bromination of 1-acetamido-2-methylnaphthalene has been studied by Shoesmith and Rubli (J.C.S. 1927, 3103) who obtained a poor yield of 4-bromo-1-amino-2-methylnaphthalene, m.p. 82° (acetyl, m.p. 223°).

5-Bromo- has m.p. 53–55° (acetyl, m.p. 184–185°) and 8-bromo-1-amino-2-methylnaphthalene, m.p. 84–85° (Vesely and Kapp, *l.c.*).

Fries and Lohmann (Ber. 1921, 54 [B], 2912) showed that 1-amino-2-methylnaphthalene sulphate is oxidised by perhydrol to 2-methyl-[a]-naphthaquinone or, by slow addition of the perhydrol, to 4:4'-diamino-3:3'-dimethyl-1:1'-dinaphthyl, m.p. 213°.

### Nitro-Amines and Diamines.

Some nitroamino derivatives of 2-methylnaphthalene have been described by Vesely

and Páč (Coll. Czech. Chem. Comm. 1930, 2, 471). From the nitration of 8-acetamido-2-methylnaphthalene at 0° in glacial acetic acid they were able to obtain 5-nitro-8-amino-2-methylnaphthalene, m.p. 183° (acetyl, m.p. 229–230°) and 7-nitro-8-amino-2-methylnaphthalene, m.p. 185° (acetyl, m.p. 219–220°). 7:8-Diamino-2-methylnaphthalene, m.p. 80–81°, gives a phenanthrazine, m.p. 295°. Similarly were prepared, from 5-acetamido-2-methylnaphthalene, 6-nitro-5-amino-, m.p. 171° (acetyl, m.p. 210–211°) and 8-nitro-5-amino-2-methylnaphthalene, m.p. 167–169° (acetyl, m.p. 202°).

By nitration of 1-acetamido-2-methylnaphthalene, Vesely and Kapp (Chem. Listy, 1924, 18, 201, 244; Rec. trav. chim. 1925, 44, 360) obtained the acetyl derivative, m.p. 240–241°, of 4-nitro-1-amino-2-methylnaphthalene, m.p. 184–185°, reduced to 1:4-diamino-2-methylnaphthalene, m.p. 111–113°. By reduction of 1:5-dinitro-2-methylnaphthalene they obtained 1-nitro-5-amino-2-methylnaphthalene, m.p. 134–135° (acetyl, m.p. 192°), and 1:5-diamino-2-methylnaphthalene, m.p. 125–128°. They also obtained 5-nitro-1-amino-2-methylnaphthalene, m.p. 136–138° (acetyl, m.p. 221–223°), by the action of concentrated sulphuric acid on 2-methyl-1-naphthylamine nitrate.

According to F. Giral (Anal. Fis. Quím. 1933, 31, 861), 1:5-diamino-2-methylnaphthalene has m.p. 136° (diacetyl, m.p. 202°), and 1:8-diamino-2-methylnaphthalene, obtained by reduction of the 1:8-dinitro-compound in aqueous suspension with phosphorus and iodine, m.p. 63° (diacetyl, m.p. 136°).

### Hydroxy Derivatives.

Several of the seven possible hydroxy derivatives of 2-methylnaphthalene are known. Fittig and Liebmann (Ber. 1887, 20, 3182) by condensing benzaldehyde with methylsuccinic acid obtained two lactic acids which by dry distillation gave two naphthols, m.p. 89° and 92° respectively, one of which should be 1- and the other 4-hydroxy-2-methylnaphthalene. 2-Methyl-1-naphthol, however, has m.p. 61°, according to Lesser (Annalen, 1914, 402, 1) who prepared it from 2-methyl-1-naphthylamine by the diazo-reaction. It is very sensitive to oxidation and was prepared in an atmosphere of carbon dioxide. Fries and Lohmann (Ber. 1921, 54 [B], 2912) studied the oxidation of 4-chloro-2-methyl-1-naphthol, m.p. 104–5° (acetate, m.p. 87°), obtained by reduction of 1-keto-2-methyl-2:3:4:4-tetrachlorotetrahydronaphthalene; it is readily converted by oxidising agents into 2-methyl-[a]-naphthaquinone. Lesser obtained 4:4'-dihydroxy-3:3'-dimethyl-1:1'-dinaphthyl, m.p. 235° (decomp.), as a by-product in the preparation of 2-methyl-1-naphthol.

6-Hydroxy-2-methylnaphthalene was obtained by Dziewoński *et al.* (*ibid.* 1925, 58 [B], 1211) from the 6-sulphonic acid; it has m.p. 128–129° (methyl ether, m.p. 78–79°). It forms a 5-nitroso derivative, m.p. 119–120°, oxidised to the 5-nitro derivative, m.p. 81–82°, which on reduction gives 5-amino-6-hydroxy-2-methylnaphthalene, m.p. 155–157° (decomp.).

7-Hydroxy-2-methylnaphthalene has m.p. 101–102° (Shreve and Lux, *l.c.*).

8-Hydroxy-2-methylnaphthalene, m.p. 109°, was first obtained by Krollpfeiffer and Schäfer (*ibid.* 1923, 56 [B], 620) from 7-methyl-1-ketotetrahydronaphthalene, which was brominated to the 2-bromo- derivative, which on heating with diethylaniline gave the desired product (cf. Ruzicka and Waldmann, *Helv. Chim. Acta*, 1932, 15, 907). The compound has also been prepared from  $\beta$ -methylnaphthalene-8-sulphonic acid (Dziewoński and Wulffsohn, *l.c.*). Veselý and Medvedeva have described 5:7-dinitro-2-methyl-8-naphthol, m.p. 166–166.5° (Coll. Czech. Chem. Comm. 1931, 3, 400). 1-Amino-2-methyl-8-naphthol was prepared by F. Giral (*Anal. Fis. Quím.* 1933, 31, 861) by the action of boiling aqueous sodium hydrogen sulphite on 1:8-dinitro-2-methylnaphthalene.

1:4-Dihydroxy-2-methylnaphthalene, m.p. 160° (diacetate, m.p. 113°), was obtained by reduction of 2-methyl- $\alpha$ -naphthaquinone by Fries and Lohmann (*l.c.*). Its 3-chloro- (diacetate, m.p. 194°) and 3-bromo- (diacetate, m.p. 209°) derivatives were also described. For some other derivatives, see F. Giral (*l.c.*).

### 2-Methylnaphthaquinones.

2-Methyl-[ $\alpha$ ]-naphthaquinone (2-methyl-1:4-naphthaquinone) has special biological interest in that it and many of its derivatives show the anti-hæmorrhagic properties of Vitamin-K (*v.* Vol. VII, 87a). It is formed by the oxidation of many 1- and 1:4-substituted 2-methyl-naphthalenes. Thus Fries and Lohmann (*l.c.*) obtained it in good yield by oxidising 4-chloro-2-methyl-1-naphthol with ferric chloride, hydrogen peroxide, chlorine or nitrous acid, although [ $\alpha$ ]-naphthaquinone is not obtained similarly from 4-chloro-1-naphthol. They also obtained it in good yield by oxidising 2-methyl-1-naphthylamine sulphate with hydrogen peroxide, and Veselý and Kapp (*Chem. Listy*, 1924, 18, 201, 244) obtained it by oxidising 2-methyl-1:4-naphthylenediamine. 2-Methyl-[ $\alpha$ ]-naphthaquinone forms long yellow needles, m.p. 104°. By the action of calcium hypochlorite it yields the 2:3-oxide, m.p. 102°, converted by warm dilute sulphuric acid into 3-hydroxy-2-methyl-[ $\alpha$ ]-naphthaquinone, m.p. 172°, reduced and acetylated to 1:3:4-triacetoxy-2-methylnaphthalene, m.p. 130° (J. Madinaveitia, *Anal. Fis. Quím.* 1933, 31, 750). G. N. Gheorghiu (*Bull. Soc. chim.* 1939, [v], 6, 493) gives m.p. 146–148° for this compound. Chlorine converts 2-methyl-[ $\alpha$ ]-naphthaquinone into 2:3-dichloro-1:4-dichloro-2-methyltetrahydronaphthalene, m.p. 45.5°, converted by hot concentrated sulphuric acid into 3-chloro-2-methyl-[ $\alpha$ ]-naphthaquinone, m.p. 153° (Fries and Lohmann, *l.c.*). The properties of 2-methyl-[ $\alpha$ ]-naphthaquinone have also been studied by Madinaveitia and de Buruaga (*Anal. Fis. Quím.* 1929, 27, 647) who obtained it by oxidising 2-methylnaphthalene with chromic acid in acetic acid and give m.p. 106°. They consider that *plumbagin* is probably 5-hydroxy-3-methyl-[ $\alpha$ ]-naphthaquinone.

The name "*menadione*" has been adopted by the American Medical Association for 2-methyl-[ $\alpha$ ]-naphthaquinone. It forms an addition compound with 1 mol. of sodium bisulphite, but when heated for a long period with sodium

bisulphite solution it gives 2-methyl-[ $\alpha$ ]-naphthaquinone-3-sulphonic acid which can be isolated as the *potassium* salt (Menotti, *J. Amer. Chem. Soc.* 1943, 65, 1209; Bochar *et al.*, *ibid.*, p. 2162).

2-Methyl-[ $\alpha$ ]-naphthaquinone can be alkylated in the 3-position by heating with a lead tetracetate in acetic acid solution in presence of a "promoter," of which malonic acid is one. The reaction can be explained by loss of carbon dioxide from the acid radical and attack by the remaining alkyl radical. Thus using lead tetracetate (or even red lead in acetic acid) 2:3-dimethyl-[ $\alpha$ ]-naphthaquinone, m.p. 126.5–127.5°, is formed, and with lead tetrapropionate, 2-methyl-3-ethyl-[ $\alpha$ ]-naphthaquinone, m.p. 73° (L. F. Fieser and F. C. Chang, *ibid.* 1942, 64, 2013). Similar alkylations can be accomplished with diacyl peroxides (L. F. Fieser and A. E. Oxford, *ibid.* 1942, 64, 2000).

2-Methylnaphthalene-5:6-quinone (6-methyl-[ $\beta$ ]-naphthaquinone) was obtained by Dziewoński *et al.* (*Ber.* 1925, 58 [B], 1211) by oxidising 5-amino-2-methyl-6-naphthol; it has m.p. 131–132°.

*Phthiocol*, the pigment of the human tubercle bacillus, is 3-hydroxy-2-methyl-[ $\alpha$ ]-naphthaquinone, m.p. 173–174°. It can be synthesised by oxidation of 2-methylnaphthalene (see R. J. Anderson and M. S. Newman, *J. Biol. Chem.* 1933, 103, 197, 405, 733; R. J. Anderson and M. M. Creighton, *ibid.* 1939, 130, 429; L. F. Fieser, *ibid.* 1940, 133, 391).

### Acyl Derivatives.

2-Methylnaphthalene is attacked by acylating agents in presence of aluminium chloride mainly in the 6-position, less in the 8-position. Thus Dziewoński and Brand (*Rocz. Chem.* 1932, 12, 693) obtained 6-acetyl-, m.p. 70–71°, 8-acetyl-, b.p. 176–180°/14 mm., and 6:8-diacetyl-2-methylnaphthalene, m.p. 127–128° (cf. G. A. R. Kon and W. T. Weller, *J.C.S.* 1939, 792). Using propionyl chloride, R. D. Haworth and F. M. Boleyn (*J.C.S.* 1932, 2248) obtained 6-propionyl-2-methylnaphthalene, m.p. 61–62°. Succinic anhydride also condenses in the 6-position (R. D. Haworth, B. M. Letsky, and C. R. Mavin, *ibid.*, p. 1784). From the acyl derivatives are obtained 2-methyl-6-, m.p. 229–230°, and 8-naphthoic acid, m.p. 147°. 2-Methyl-1-naphthoic acid, m.p. 126–127°, has been prepared by Mayer and Sieglitz (*Ber.* 1922, 55 [B], 1851) and several other workers. 1-Benzoyl-2-methylnaphthalene, from the naphthoyl chloride and benzene with aluminium chloride, has m.p. 74°. 2-Methyl-1-naphthonitrile has m.p. 87–88° (R. C. Fuson *et al.*, *J. Amer. Chem. Soc.* 1941, 63, 2648).

### ETHYLNAPHTHALENES.

The ethylation of naphthalene by means of ethylene in presence of a phosphoric acid catalyst at 250–300° has been observed by B. W. Malishev (*ibid.* 1935, 57, 883) and by V. N. Ipatieff, H. Pines, and V. I. Komarevsky (*Ind. Eng. Chem.* 1936, 28, 222) but no individual compounds were isolated from the mixed product. The condensation of ethylene with naphthalene in the presence of aluminium

chloride to give mono- and poly-ethylnaphthalenes is described by I.G. (B.P. 265601). Milligan and Reid obtained an ethylnaphthalene by warming naphthalene with diethylbenzene and aluminium chloride (J. Amer. Chem. Soc. 1922, 44, 206).

$\alpha$ -Ethylnaphthalene was prepared by Fittig and Remsen (Annalen, 1870, 155, 118) from  $\alpha$ -bromonaphthalene, ethyl bromide, and sodium but their product did not solidify. By catalytic reduction of 1-acetylnaphthalene, G. Lévy (Compt. rend. 1931, 193, 174) obtained a purer product, m.p. 15° (see Table V).

By nitration of 1-ethylnaphthalene in acetic acid at 3–10°, Lévy (Compt. rend. 1935, 201, 900) obtained a mixed product from which, after reduction, he isolated 4-ethyl- $\alpha$ -naphthylamine as an oil (acetyl, m.p. 148.5°) the sulphate of which was converted by 1% sulphuric acid at 900° into 4-ethyl- $\alpha$ -naphthol, m.p. 42°, which he had previously synthesised (*ibid.* 1933, 197, 772). Baddar and Warren (J.C.S. 1938, 401), give 151° as the m.p. of 4-ethyl-acet- $\alpha$ -naphthalide. Lévy also studied the hydrogenation of 1-ethylnaphthalene (Compt. rend. 1931, 193, 174). 1-Ethyl-2-naphthol has m.p. 105° (K. Dzięwoński and

TABLE V.—ETHYLNAPHTHALENES.

Orientation.	B.p.	M.p.	Picrate, m.p.	Source.	Reference.
1-Ethyl	251–252°  256.5°/756 mm.  112–116°/9 mm.	Below –14°  15°	  98.5°	$\alpha$ -Bromonaphthalene, Na and EtBr. 1-Acetylnaphthalene. 1-Acetylnaphthalene.	Fittig and Remsen, Annalen, 1870, 155, 118. G. Lévy, Compt. rend. 1931, 193, 174. Fröschl and Harlass, Monatsh. 1932, 59, 275.
2-Ethyl	  117–118°/10 mm.  252°/760 mm.  170–172°/50 mm.  257–258°/760 mm.	     –7 to –6.5°	69°  72–73°  72°  72°  76.5–77°	$\beta$ -Bromonaphthalene, Na and EtBr. Synthesis. Coal tar.  2:2-Diethyltetralin. 2-Acetylnaphthalene.	Brunel, Ber. 1884, 17, 1179. Barbot, Bull. Soc. chim. 1930, [iv], 47, 1314. Kruber and Schade, Ber. 1936, 69 [B], 1722. Sengupta, J. pr. Chem. 1938, [ii], 151, 96. Lévy, Ann. Chim. 1938, [xi], 9, 5.

C. Dragan, Bull. Acad. Polonaise, 1934, A, 398).

1-Vinylnaphthalene is formed by the action of hot potassium hydroxide on 1- $\beta$ -hydroxyethylnaphthalene at a low pressure. It boils at 126–128°/15 mm. with resinification, and forms a picrate, m.p. 101–102° (W. Palfray, S. Sabetay, and D. Sontag, Compt. rend. 1932, 194, 2065). 2-Vinylnaphthalene has b.p. 135–137°/18 mm., m.p. 66° (D. Sontag, *ibid.* 1933, 197, 1130). The use of 1- and 2-vinylnaphthalenes for the preparation of resins suitable for lacquers has been claimed (I.C.I., B.P. 355032; cf. M. M. Koton, J. Gen. Chem. Russ. 1939, 9, 1626).

$\beta$ -Ethylnaphthalene was prepared by Brunel (Ber. 1884, 17, 1179) by the method of Fittig from  $\beta$ -bromonaphthalene, ethyl bromide, and sodium, and also by the action of ethyl bromide on naphthalene in presence of aluminium chloride, a method also used by Marchetti (Gazzetta, 1881, 11, 265, 439). It is probable, however, that the product obtained by the latter method contained the  $\alpha$ -isomer. More recently Lévy has obtained a product which, from its melting-point and that of its picrate, appears to be purer than that obtained by the earlier workers (see Table V). He prepared 2-acetylnaphthalene by the Friedel-Crafts process, using nitrobenzene as solvent, and reduced this with hydrogen and a nickel-pumice catalyst. Barbot prepared 2-ethylnaphthalene by dehydrogenating 2-ethyl-5:6:7:8-tetrahydronaphthalene with sulphur (Bull. Soc. chim. 1930, [iv], 47, 1314).

2-Ethylnaphthalene was separated as its picrate by Kruber and Schade (see Table) from a coal-tar fraction, b.p. 250–254°.

Substitution products of 2-ethylnaphthalene have been described in a series of papers by G. Lévy (Compt. rend. 1932, 194, 1749, 1952; 195, 801; 1936, 202, 1679; 203, 337) and most of his work is summarised in a later paper (Ann. Chim. 1938, [xi], 9, 5). Nitration in acetic acid at 3–10° gives the 1-nitro-, m.p. 49.5–50°, and the 8-nitro-compound, not obtained pure, which were reduced to the 2-amino-, m.p. 25–28° (acetyl, m.p. 156.5°), and the 8-amino-compound (acetyl, m.p. 148.5–149°).

Sulphonation of 2-ethylnaphthalene with concentrated sulphuric acid at 95° gives the 6-sulphononic acid (chloride, m.p. 65–65.5°; amide, m.p. 190–191°) characterised by conversion into 2-ethyl-6-naphthol, m.p. 97–98° (methyl ether, m.p. 58°), which was also synthesised from  $\gamma$ -p-methoxybenzyl- $n$ -valeric acid. Other ethylnaphthols described by Lévy are 2-ethyl-1-naphthol, m.p. 69.5–70°, from the 1-amine and also by synthesis; 2-ethyl-4-naphthol, m.p. 50.5–51°, by synthesis; 2-ethyl-7-methoxynaphthalene, m.p. 51–52°; and 2-ethyl-8-naphthol, m.p. 56.5–57°, from the amine and by synthesis.

$\beta$ -Naphthylethyl alcohol, m.p. 67.5–68°, is obtained from  $\beta$ -naphthyl magnesium bromide. When heated with potassium hydroxide it gives 2-vinylnaphthalene, m.p. 66°, b.p. 135–137° (D. Sontag, Compt. rend. 1933, 197, 1130).

Oxidation of 2-ethylnaphthalene with chromic-



acetic acid gives 2-ethyl-[ $\alpha$ -]naphthaquinone, m.p. 88° (Kruber and Schade, Ber. 1936, 69 [B], 1722).

According to R. Kuhn and K. Wallenfels (*ibid.* 1939, 72 [B], 1407), the sea urchin *Arbacia pustulosa* secretes a substance, *Echinochrome A*, to attract the spermatozoa; this is a quinone derived from heptahydroxy-2-ethylnaphthalene.

### PROPYLNAPHTHALENES.

The two *n*-propylnaphthalenes were prepared by Bargellini and Melacini (Atti. R. Accad. Lincei, 1908, [v], 17, 26) by reducing  $\alpha$ - and  $\beta$ -propionynaphthalenes, and they recorded the melting-point of the *picrates* as  $\alpha$ -, 141–142°;  $\beta$ -, 90–92°. Roblin, Davidson, and Bogert (*l.c.*) prepared 1-*n*-propylnaphthalene by dehydrogenating 5-propyltetralin, and obtained from it a *picrate*, m.p. 91–92°. They then repeated Bargellini and Melacini's preparation from  $\alpha$ -propionynaphthalene, reducing the ketone by the Clemmensen process, and again obtained 1-*n*-propylnaphthalene *picrate*, m.p. 92°. It would therefore appear that the melting-points recorded by Bargellini and Melacini should be interchanged.

Direct introduction of propyl groups into naphthalene using a propyl-compound and a catalyst proceeds with considerable ease. Whether a *n*-propyl or isopropyl-compound is used as reagent, the product is an isopropylated naphthalene, although there may be some *n*-propyl derivative present (*see* Haworth, Letsky, and Mavin, J.C.S. 1932, 1784). Moreover, substitution occurs mainly in the  $\beta$ -position of naphthalene.

H. Meyer and K. Bernhauer (Monatsh. 1929, 53–54, 741) studied the reaction between naphthalene and isopropyl alcohol in 80% sulphuric acid at about 80°. After removal of the sulphonic groups from the product, the hydrocarbons were fractionated into mono-, di-, tri-, and tetra-isopropylnaphthalenes. The mono- was mainly  $\beta$ - with some  $\alpha$ -; the di- contained 2:6-, 2:7-, and 1:6- (m.p. 52°) di-isopropylnaphthalene; there was some tri-, and a tetra-isopropylnaphthalene, m.p. 127°. The same tetra derivative was obtained by I.G. (B.P. 316951) by condensing propylene with naphthalene in contact with fuller's earth at 120–180°, and also by passing propylene into naphthalene containing aluminium chloride at 80° (B.P. 295990); Calcott, Tinker, and Weinmayr (J. Amer. Chem. Soc. 1939, 61, 1010) obtained it using hydrogen fluoride as condensing agent. Tsukerwanik and Terentieva (J. Gen. Chem. Russ. 1937, 7, 637), by the action of isopropyl alcohol on naphthalene in ligroin in the presence of aluminium chloride on a water bath, obtained a mixture containing 32.6% of  $\beta$ -, 15.4% of di-, and 10.7% of tri-isopropylnaphthalenes. They state that any  $\alpha$ -compound present is changed into  $\beta$ - during distillation.

Condensation of  $\alpha$ -naphthol with propionic acid-zinc chloride, followed by Clemmensen reduction, gives 2-*n*-propyl-1-naphthol, m.p. 113° (Desai and Warawdekar, Proc. Indian Acad. Sci. 1941, 13, A, 33, 39). R. W. Stoughton, however, gives m.p. 51–52° for this compound (J. Amer. Chem. Soc. 1935, 57, 204).

2-*n*-Propyl-[ $\alpha$ -]naphthaquinone, m.p. 39–39.5°, has been prepared by Fieser, Campbell, and Fry (*ibid.* 1939, 61, 2213).

$\alpha$ -isoPropylnaphthalene was prepared by Herzenberg and von Winterfeld (Ber. 1931, 64 [B], 1043) from 1-acetylnaphthalene and methyl magnesium iodide; it had b.p. 132–134°/10 mm., *picrate*, m.p. 85–86°. J. W. Cook (J.C.S. 1932, 466) prepared it in a similar manner from ethyl  $\alpha$ -naphthoate, and gave b.p. 263–264°/760 mm., *picrate*, m.p. 83.5–86°. The intermediately formed 1-isopropylnaphthalene gave a *picrate*, m.p. 88–89° (cf. Grignard, Bull. Soc. chim. 1901, [iii], 25, 498, who gave m.p. 91°). When treated with acids, the isopropenyl-compound forms a dimeride, m.p. 198.5–199.5°. 1-*a*-Hydroxyiso-propylnaphthalene has m.p. 96°. Roblin, Davidson, and Bogert (*l.c.*) also prepared 1-isopropylnaphthalene by dehydrogenating 5-isopropyltetralin.

1-isoPropylnaphthalene-4-sulphonic acid forms an aniline salt, m.p. 190° (decomp.); and may be converted into 1-isopropyl-4-naphthol, m.p. 72° (Meyer and Bernhauer, *l.c.*).

2-isoPropylnaphthalene has been obtained by a number of different methods. R. D. Haworth, Letsky, and Mavin (*l.c.*) used two methods; they condensed isopropyl bromide with naphthalene in presence of aluminium chloride, and also used the Grignard method starting from 2-acetylnaphthalene. Both methods gave a product of b.p. 130–135°/12 mm., *picrate*, m.p. 93–95°. By the first method using *n*-propyl bromide they obtained a less pure product giving a *picrate*, m.p. 89–90°, which they considered contained some 2-*n*-propylnaphthalene. Ruzicka and Capato (Annalen, 1927, 453, 62), using the Grignard method with ethyl  $\beta$ -naphthoate, obtained a product, b.p. 126–127°/12 mm., *picrate*, m.p. 91°; Barbot (Bull. Soc. chim. 1930, [iv], 47, 1314) dehydrogenated 6-isopropyltetralin, and obtained a *picrate*, m.p. 89–90°. Cook (*l.c.*) using the same method as Haworth *et al.*, gives the b.p. 263–265°, m.p. of *picrate* 93–95°. Price and Ciskowski obtained  $\beta$ -isopropylnaphthalene from naphthalene and  $\beta$ -isopropyl alcohol using boron trifluoride as condensing agent (J. Amer. Chem. Soc. 1938, 60, 2499).

Sulphonation of 2-isopropylnaphthalene gives the 1-sulphonic acid, m.p. 137° (decomp.) (*chloride*, m.p. 61°; *amide*, m.p. 140°). When naphthalene-2-sulphonic acid and *n*-propyl alcohol are treated with concentrated sulphuric acid at 120°, 1:6-di-isopropylnaphthalene-3 (or 7)-sulphonic acid is formed (*chloride*, m.p. 71°; *amide*, m.p. 179–180°) from which a 1:6-di-isopropyl- $\beta$ -naphthol, m.p. 90°, is prepared. Similarly naphthalene-1-sulphonic acid gives a di-isopropylnaphthalenesulphonic acid (*chloride*, m.p. 119°; *amide*, m.p. 151°) from which a di-isopropylnaphthalene, m.p. 38°, is obtained (Meyer and Bernhauer, *l.c.*). 2-isoPropyl-1-naphthol has m.p. 65–66°.

For the preparation of isopropylnaphthalene-sulphonic acids for use as wetting agents, *see* Badische (G.P. 336558, 1917). "Nekal BX," the well-known wetting agent, is said to be a di-isopropyl-naphthalenesulphonic acid salt.



## BUTYLNAPHTHALENES.

1- and 2-*n*-Butylnaphthalenes were prepared by Bargellini and Melacini (*l.c.*) by reducing the corresponding naphthyl *n*-propyl ketones; 1-*n*-butylnaphthalene has b.p. 281–283°, *picrate*, m.p. 104–106°, and the 2-isomer, b.p. 283–285°, *picrate*, m.p. 73–74°.

1-*sec*-.Butylnaphthalene, b.p. 105–107°/2 mm., *picrate*, m.p. 76°, is formed, according to Tsukervanik and Terentieva, along with di-*sec*-.butylnaphthalenes, when naphthalene is condensed with *sec*-.butyl chloride in the presence of aluminium chloride.

The 1- and 2-isobutylnaphthalenes were prepared by Darzens and Rost (*Compt. rend.* 1908, 146, 933) by reducing 1- and 2-naphthyl *iso*-propyl ketones; they have b.p. 136–138°/11 mm. and 112–113°/6 mm. respectively.

Several workers have studied the *tert*-.butylnaphthalenes, and it is impossible to refer to all their work. Condensation of naphthalene with *iso*- or *tert*-.butyl compounds give *tert*-.butylnaphthalenes, probably because the active agent is in both cases isobutylene. Assuming that the naphthalene undergoes  $\beta$ -substitution, it follows that the product obtained by Fieser and Price (*J. Amer. Chem. Soc.* 1936, 58, 1841) from naphthalene and 1 mol. of *tert*-.butyl chloride in the presence of a small amount of aluminium chloride is  $\beta$ -*tert*-.butylnaphthalene, b.p. 127–131°/9 mm., *picrate*, m.p. 99.5–100.5°. Barbot (*l.c.*) obtained a product giving a *picrate* of almost the same m.p., 102–103°, by dehydrogenating *tert*-.butyltetralin. Fieser and Price also obtained two di-*tert*-.butylnaphthalenes, one of m.p. 86–90° (*picrate*, m.p. 155.5–156.5°), the other m.p. 146–147°, not forming a *picrate*.\* According to Tsukervanik and Terentieva (*l.c.*), *tert*-.butyl alcohol with naphthalene and aluminium chloride forms both 1- and 2-*tert*-.butylnaphthalene, the melting-point of the *picrates* being 92–93° and 84–85° respectively. The products were orientated by oxidation by dilute nitric acid at 150–180° to the 1- and 2-naphthoic acids. It may provisionally be assumed that their products were not pure. They also obtained a di-*tert*-.butylnaphthalene, m.p. 132° (*picrate*, m.p. 99°).

N. K. Bromby, A. T. Peters, and F. M. Rowe (*J.C.S.* 1943, 144) have confirmed the results obtained by Fieser and Price. They condensed naphthalene with *tert*-.butyl chloride in the presence of zinc chloride at 95–105°, and obtained  $\beta$ -*tert*-.butylnaphthalene as a colourless, steam volatile liquid with a pleasant aromatic odour, b.p. 274–278°, *picrate*, m.p. 100–101.5°. It did not form a styphnate. By oxidation with chromic acid it gives 2-*tert*-.butyl-[ $\alpha$ ]-naphthaquinone, pale yellow leaflets from ligroin, m.p. 76–77°. C. L. Price and J. M. Ciskowski (*J. Amer. Chem. Soc.* 1938, 60, 2499) obtained  $\beta$ -isopropyl- and  $\beta$ -*tert*-.butyl-naphthalene by condensing naphthalene with the corresponding alcohol in the presence of boron trifluoride.

Butylnaphthols have been obtained by isomerisation of naphthyl *n*-butyrates followed by reduction of the products. 1-*Butyl*-2-naphthol thus obtained has m.p. 80–81° (Gulati, Seth, and Venkataram, *J. pr. Chem.* 1933, [ii], 137, 50) and 2-*butyl*-1-naphthol, m.p. 71–72° (Stoughton, *J. Amer. Chem. Soc.* 1935, 57, 202). According to Tschitschibabin, 1-*tert*-.butyl-2-naphthol has m.p. 113° (*Bull. Soc. chim.* 1935, [v], 2, 515).

The salts of butylnaphthalene sulphonic acids in aqueous solution have the properties of wetting agents. They are prepared by the action of *n*-butyl alcohol on naphthalene or its  $\beta$ -sulphonic acid in concentrated sulphuric acid (B.P. 246817; for their use as wetting agents, see B.P. 319083; 342399; I.G., G.P. 459605; 496102), and find application in the textile industries and in insecticidal preparations.

## DIMETHYLNAPHTHALENES AND THEIR DERIVATIVES.

In Table II are summarised some constants of the dimethylnaphthalenes, the melting-point of *picrates* and styphnates and literature references. The word "synthesis" in the fifth column indicates that the compound has been prepared by one of the many syntheses involving ring closure of a benzene derivative, usually with intermediate formation of a tetralin derivative. Some further notes, including reference to some of the derivatives which have been described, follow.

(i) 1:2-Dimethylnaphthalene.—When  $\beta$ -metylnaphthalene is treated with trioxymethylene in acetic-hydrochloric acid, 1-chloromethyl-2-metylnaphthalene, m.p. 65°, is obtained, reduced to 1:2-dimethylnaphthalene. Bromination of 1:2-dimethylnaphthalene gives the 4-bromo derivative, m.p. 39–40°, and chloromethylation gives the 4-chloromethyl derivative, m.p. 70–71° (Hewett, *J.C.S.* 1940, 299).

(ii) 1:3-Dimethylnaphthalene.—This compound was prepared by M. C. Kloetzel starting from  $\beta$ -benzoylpropionic acid; the same substance was used in the synthesis of 1:2- and 1:4-dimethylnaphthalenes.

(iii) 1:4-Dimethylnaphthalene.— $\alpha$ -Metylnaphthalene with trioxymethylene in acetic-hydrochloric acid gives 4-chloromethyl-1-metylnaphthalene, m.p. 62°, reduced to 1:4-dimethylnaphthalene. The nitration of 1:4-dimethylnaphthalene was studied by Robinson and Thompson (*ibid.* 1932, 2015), who found that, nitrating at a low temperature in acetic anhydride and nitromethane, nitration occurs in the methyl group giving  $\omega$ -nitro-1:4-dimethylnaphthalene, m.p. 107°; an unidentified dinitro-compound, m.p. 128°, was also isolated. The corresponding  $\omega$ -amino-compound gives an *acetyl* derivative, m.p. 142°;  $\omega$ -hydroxy, m.p. 77°,  $\omega$ -bromo-compound, m.p. 80°.

(iv) 1:5-Dimethylnaphthalene.—By treating naphthalene (I.G., B.P. 345146) or 1-chloromethylnaphthalene with formaldehyde and hydrochloric acid (Anderson and Short, *J.C.S.* 1933, 485) a mixture of di(chloromethyl)-naphthalenes is obtained, melting at 130–140°

\* In later work, Price, Shafer, Huber, and Bernstein obtained, besides the di-*tert*-.butylnaphthalene, m.p. 145–146°, a product, m.p. 80–82°, which formed a *picrate* and which, by careful recrystallisation from acetic acid, gave a new di-*tert*-.butylnaphthalene, m.p. 103–104° (*J. Org. Chem.* 1942, 7, 517).

(I.G.) or 130–145° (Anderson and Short), from which the latter authors could not separate an individual compound. After reduction with zinc and hydrochloric acid, however, they were able to isolate from the mixed dimethylnaphthalenes a sample of pure 1:5-dimethylnaphthalene, identical with that prepared by Veselý and Štursa.

(v) 1:6-Dimethylnaphthalene was isolated by Weissgerber and Kruber from a heavy fraction of coal-tar distillate, b.p. 260–265°, by cold sulphonation. The sparingly soluble sulphonic acid obtained was crystallised from 33% sulphuric acid and the sulphonic group afterwards removed by hydrolysis. 1:6-Dimethylnaphthalene-4-sulphonamide has m.p. 185°. By alkaline fusion the sulphonic acid gives 1:6-dimethyl-4-naphthol, m.p. 82°. 2:5-Dimethyl-naphthaquinone has m.p. 95°.

5:8-Diacetoxy-1:6-dimethylnaphthalene was obtained by Heilbron and Wilkinson (J.C.S. 1930, 2546) by oxidising 1:2:5-trimethylnaphthalene with chromic acid in 80% acetic acid.

(vi) 1:7-Dimethylnaphthalene. — This compound was obtained by Veselý and Medvedeva by a long process from 5:7-dinitro-2-methyl-8-naphthol, which was converted successively into the 8-chloro-compound, the 8-malonate, 8-acetate, and finally to 5:7-dinitro-2:8-dimethyl- (=2:4-dinitro-1:7-dimethyl)naphthalene, m.p. 163–165.5°. By reduction this gave 2:4-diamino-1:7-dimethylnaphthalene, m.p. 114–116°, deaminated by nitrous acid and alcohol to 1:7-dimethylnaphthalene. The authors also described 2-nitro-4-amino, m.p. 151–153°, 2-nitro-, m.p. 56.5–58°, and 2-amino-1:7-dimethylnaphthalene (acetyl derivative, m.p. 207–208°) and 1:7-dimethyl-2-naphthol, m.p. 138–140°.

O. Kruber and W. Schade described in detail the isolation of 1:7-dimethylnaphthalene from a coal-tar fraction, b.p. 258–260°, from which the 1:6-isomer had been previously removed. The fraction was treated ten times with one-tenth its weight of concentrated sulphuric acid at 45°. From the fifth to eighth sulphonations was isolated 1:7-dimethylnaphthalene-4-sulphonic acid (amide, m.p. 204–205°), giving 1:7-dimethylnaphthalene by acid hydrolysis, and 1:7-dimethyl-4-naphthol, m.p. 102°, by alkaline fusion (Ber. 1936, 69 [B], 1722).

(vii) 2:3-Dimethylnaphthalene was first discovered in coal tar by Weissgerber (l.c.). Later Kruber sulphonated a coal-tar oil, b.p. 265–267°, from which the 1:6-, 2:6-, and 2:7-isomers had been removed, and isolated 2:3-dimethylnaphthalene-6-sulphonic acid (amide, m.p. 228–229°). By hydrolysis he obtained 2:3-dimethylnaphthalene, 5% yield on the starting material. He also described 2:3-dimethyl-6-naphthol, m.p. 160°, 2:3-dimethyl-[ $\alpha$ ]-naphthaquinone, m.p. 127°, and 6:7-dimethyl-[ $\beta$ ]-naphthaquinone, m.p. 146–147°. 6:7-Dimethyl-[ $\alpha$ ]-naphthaquinone has m.p. 118–119° (Fieser, Campbell, and Fry, J. Amer. Chem. Soc. 1939, 61, 2206).

2:3-Dimethylnaphthalene was first synthesised by Schroeter, Lichtenstadt, and Irieneu and shown to be identical with *guaiene*, a product of dry distillation of *guaiacum* resin. *Pyroguaiacin*

is 6-hydroxy-7-methoxy-2:3-dimethylnaphthalene (Ber. 1918, 51, 1604).

Sulphonation of 2:3-dimethylnaphthalene by concentrated sulphuric acid at 40–50° or by chlorosulphonic acid in carbon tetrachloride cold gives mainly the 5-sulphonic acid (amide, m.p. 206°) and some of the 6-sulphonic acid. From the 5-sulphonic acid, 2:3-dimethyl-5-naphthol, m.p. 140°, was prepared (E. A. Coulson, J.C.S. 1938, 1305). The same author has studied the hydrogenation of 2:3-dimethylnaphthalene.

2:3-Dimethylnaphthalene condenses with succinic anhydride in the presence of aluminium chloride to give 2:3-dimethyl-6-naphthoylpropionic acid, m.p. 179–180°, which by fusion with potassium hydroxide gives 2:3-dimethyl-6-naphthoic acid, m.p. 254–255° (methyl ester, m.p. 147–148°; R. D. Haworth and F. M. Bolam, *ibid.* 1932, 2248).

(viii) 2:6-Dimethylnaphthalene. — This was obtained from coal tar by Weissgerber and Kruber (l.c.) by sulphonating at 135–140° the same coal-tar fraction from which the 1:6-isomer was obtained, and pouring on to ice, when a sparingly soluble sulphonic acid separated which by hydrolysis gave 2:6-dimethylnaphthalene. Three individual sulphonic acids of 2:6-dimethylnaphthalene have been described. Sulphonation in the cold (Weissgerber and Kruber, l.c.) or in an indifferent solvent at 50° (I.G., B.P. 462664) gives the 8-sulphonic acid (chloride, m.p. 107–108°; amide, m.p. 206–207°). Sulphonation with concentrated sulphuric acid at 135–140°, or at 110° for 14 hours, or heating the 1-sulphonic acid with 90% sulphuric acid at 115–120° for 14 hours (I.G., B.P. 462337) gives the 7- (or 3-) sulphonic acid (chloride, m.p. 62–63°; amide, m.p. 265–266°) (cf. Veselý and Štursa, Coll. Czech. Chem. Comm. 1932, 4, 21). By sulphonating for a short time at 110–120° with monohydrate, chlorosulphonic acid, or oleum, the 1-sulphonic acid is said to be formed (chloride, m.p. 116–117°; amide, m.p. 124–125°; I.G., B.P. 461894). By fusing these sulphonic acids with alkali the following naphthols are obtained: 2:6-dimethyl-8-naphthol, m.p. 105–106°; -7-naphthol, m.p. 174°; -1-naphthol, m.p. 113°. However, Veselý and Štursa prepared 2:6-dimethyl-1-naphthol from the 1-amino-compound, m.p. 91°, of F. Mayer and E. Alken (Ber. 1922, 55 [B], 2278) and found m.p. 133°.

By nitration of 2:6-dimethylnaphthalene, Mayer and Alken obtained the 1-nitro-compound, m.p. 68°, two dinitro derivatives, m.p. 179° and 186°, and a trinitro derivative, m.p. 243°. By nitration of the 1-amine, m.p. 91°, Veselý and Štursa obtained 4-nitro-1-amino-2:6-dimethylnaphthalene, m.p. 194–195° (acetyl, m.p. 200°) whence they prepared 4-nitro-2:6-dimethylnaphthalene, m.p. 84–85°, and 4-amino-2:6-dimethylnaphthalene, m.p. 93–49° (acetyl, m.p. 207–208°). Numerous other derivatives are described by the authors quoted. With sulphonyl chloride, 2:6-dimethylnaphthalene gives a *monochloro*, b.p. 293–297°, and a *dichloro* derivative, m.p. 135° (I.G., B.P. 263844).

2:6-Dimethyl-3(=7)-naphthylamine, m.p. 129° (acetyl, m.p. 231°), was prepared by Coulson (J.C.S. 1934, 1411) from the corresponding naphthol by the Bucherer reaction; he also

prepared the 3-naphthonitrile, m.p. 160°, and the 3-naphthoic acid, m.p. 228° (chloride, m.p. 79°; anilide, m.p. 238°).

2:6-Dimethyl-[ $\alpha$ ]-naphthaquinone has m.p. 136–137°, and the [ $\beta$ ]-quinone, m.p. 151–152° (Weissgerber and Kruber, l.c.).

(ix) 2:7 - Dimethylnaphthalene. — Detailed directions for the separation of this hydrocarbon, through its sulphonic acid, from coal-tar heavy oil, are given by Weissgerber and Kruber (l.c.). Sulphonation of the hydrocarbon at 100° gives the 3-sulphonic acid (amide, m.p. 197–198°). 2:7-Dimethyl-3-naphthol has m.p. 171–172°. Coulson (*ibid.* 1935, 79) converted this by the Bucherer reaction into 2:7-dimethyl-3-naphthylamine, m.p. 139° (acetyl, m.p. 207°), and into the 3-naphthonitrile, m.p. 145°, and 3-naphthoic acid, m.p. 224° (chloride, m.p. 70°; anilide, m.p. 207–208°).

2:7-Dimethyl-[ $\alpha$ ]-naphthaquinone has m.p. 114–115°, and the [ $\beta$ ]-quinone, m.p. 152–153° (Weissgerber and Kuber, l.c.).

### TRIMETHYLNAPHTHALENES.

The constants of the 14 isomeric trimethylnaphthalenes are given, with references, in

Table III. All have been synthesised; for the methods used the original papers must be consulted. Several authors isolated a dimethyl- and a trimethyl-naphthalene by dehydrogenating sapogenin, amylin, and other substances of vegetable origin now classified as triterpene derivatives. It was shown by Ruzicka and Ehmman that the dimethylnaphthalene is 2:7-, and the trimethylnaphthalene, *sapotalin*, the 1:2:7- derivative (Helv. Chim. Acta, 1932, 15, 431). The constitution of *sapotalin* was determined independently by Späth and Hromatka (Monatsh. 1932, 60, 117). An account of the many different substances which give *sapotalin* by heating with selenium at 300–350° is given by Ruzicka and collaborators (Helv. Chim. Acta, 1932, 15, 431); these include hederagenin, sumaresinolic acid, siarsinolic acid, betulin, *ascigenin*, oleanolic acid, and cyclamiretin.

Another trimethylnaphthalene, 1:2:5-, was obtained from a product of animal origin, the "tetracyclosqualene" from the unsaponifiable matter of elasmobranch fish oils, by Heilbron, Harvey, and Kamm (J.C.S. 1926, 3136), its identity being established by Heilbron and Wilkinson (*ibid.* 1930, 2546) and the same

TABLE VI.—METHYLETHYLNAPHTHALENES.

Orientat on.	B.p.	M.p.	(a) Picrate, (b) Styphnate, m.p.	Source.	Reference.
1-Me-4-Et.	122°/40 mm.		(a) 98–99°	4-Acetyl-1-methyl-	Dziewoński and Marusińska, Bull. Acad. Polonaise 1933, A, 316.
1-Me-5-Et.		40°	(a) 97°	Synthesis.	Harvey, Heilbron, and Wilkinson, J.C.S. 1930, 423.
1-Me-6-Et.	140°/12 mm. 146°/14 mm.		(a) 82° (a) 80–81° (b) 88·5–89·5°	Synthesis. Synthesis.	<i>Idem, ibid.</i> Pope and Bogert, J. Org. Chem. 1938, 2, 276.
1-Me-7-Et.	133°/12 mm. 134·5–136°/12 mm.		(a) 97° (a) 95–96° (b) 126° (a) 96° (b) 126°	Synthesis. Alanto-lactone. Artemisin (v. Vol. I, 497a) from <i>Artemisia maritima</i> .	Harvey, Heilbron, and Wilkinson, l.c. Ruzicka and Van Melssen, Helv. Chim. Acta, 1931, 14, 397. Tettweiler, Engcl, and Wedekind, Annalen, 1932, 492, 108.
2-Me-3-Et.	262°/725 mm.			6-Methyltetralin.	P. Karrer and A. Epprecht, Helv. Chim. Acta, 1940, 23, 275.
2-Me-5-Et.	135–138°/12 mm.		(a) 81·5°	Synthesis.	Brunner and Grof, Monatsh. 1934, 64, 28.
2-Me-6-Et.		44–45°	(a) 100–101° (b) 138–139° (a) 109° (b) 119°	Synthesis. 6-Acetyl-2-methyl-	Brunner and Grof, <i>ibid.</i> 1935, 66, 433. Kon and Weller, J.C.S. 1939, 792.
2-Me-8-Et.	128°/11 mm.		(a) 106° (a) 106° (b) 143–144°	Synthesis. 8-Acetyl-2-methyl-	Brunner and Grof, Monatsh. 1934, 64, 28. Kon and Weller, J.C.S. 1939, 793.
DIETHYLNAPHTHALENE.					
1:4-Diethyl.	136–139°/8 mm.		(a) 82–83°	Reduction of 4-acetyl-1-ethyl-	Fröschl and Harlass, Monatsh. 1932, 59, 275.

TABLE VII.—METHYLISOPROPYLNAPHTHALENES.

Name.	B.p.	M.p.	(a) Pterate, (b) Styphnate, m.p.	Source.	Reference.
1-Me:4-Pr $\beta$ .	135-145°/12 mm. 148°/16 mm.		(a) 99-100° (a) 100-101°	Synthesis. Synthesis.	Ruzicka and M. Mingazzini, <i>Helv. Chim. Acta</i> , 1922, 5, 714. Barnett and Cook, <i>J.C.S.</i> 1933, 22.
1-Me:7-Pr $\beta$ (Eudalene).	140°/11 mm. 152°/18 mm. 281°		(a) 91° (b) 119°  (a) 92.8° (corr.)  (a) 95° (b) 122°	Selinene. Eudesmol. Synthesis. Synthesis.	Ruzicka and Stoll, <i>Helv. Chim. Acta</i> , 1922, 5, 923. Ruzicka and Capato, <i>Annalen</i> , 1927, 453, 62. G. Darzens and A. Levy, <i>Compt. rend.</i> 1932, 194, 2056. Barnett and Sanders, <i>J.C.S.</i> 1933, 434.
2-Me:8-Pr $\beta$ (1-Pr $\beta$ :7-Me) Apocadalene.	139-140°/12 mm. 282°		(a) 101-102° (b) 103-104° (a) 102° (b) 106°	Cadalene. Synthesis.	Ruzicka and Mingazzini, <i>l.c.</i> Barnett and Sanders, <i>l.c.</i>
1:4-Dimethyl-6-isopropyl.	155-157°/12 mm.		(a) 102.5-103°	Synthesis.	Ruzicka <i>et al.</i> , <i>Helv. Chim. Acta</i> , 1933, 16, 268.
1:5-Dimethyl-7-isopropyl.	110-112°/0.8 mm.		(a) 115.5-116.5°	Synthesis.	<i>Idem, ibid.</i>
1:6-Dimethyl-4-isopropyl (Cadalene).	155-160°/15 mm. 155-156°/11 mm.		(a) 115° (b) 139°  (a) 114-115° (b) 139° (a) 114-115° (b) 140°	Cadinene, isozingiberene. Synthesis. Synthesis.	Ruzicka and Meyer, <i>ibid.</i> 1921, 4, 508. Ruzicka and F. Seldel, <i>ibid.</i> 1922, 5, 369. Barnett and Cook, <i>J.C.S.</i> 1933, 22.
1:7-Dimethyl-4-isopropyl.		60°	(a) 92° (b) 120°	Synthesis.	Rapson and Short, <i>ibid.</i> 1933, 128.

hydrocarbon was obtained by Ruzicka and Hosking by heating agathidicarboxylic acid, which is present in kauri copal and in hard and soft manila resins, with sulphur at 180° (*Helv. Chim. Acta*, 1930, 13, 1402). All this work on natural products led to the synthesis of the trimethylnaphthalenes, eleven by Ruzicka and his co-workers, the others by Heilbron and Wilkinson (*see especially* Ruzicka and Elmann, *l.c.*). These hydrocarbons are best characterised by their styphnates, since the pterates, according to Ruzicka, do not always show depression of melting-point in admixture with one another.

Ruzicka and collaborators have synthesised the five isomeric methoxy derivatives of 1:2:7-trimethylnaphthalene; their melting-points are: 3-methoxy, 69-70°; 4-methoxy, 89-90°; 5-methoxy, 81-82°; 6-methoxy, 83-84°; 8-methoxy, b.p. 151-153°/9 mm. (*ibid.* 1936, 19, 322, 343, 370). Kruber (*Ber.* 1939, 72 [B], 1972) prepared 1:3:7-trimethyl-6-naphthol, m.p. 95-96°, from the corresponding sulphonic acid. He also converted 1:3:7-trimethylnaphthalene into the 5:6-quinone, m.p. 154-155°, and the 5:8-quinone, m.p. 136-137°. When 2:3:6-trimethylnaphthalene is oxidised with chromic acid it gives both the [a]-quinone, m.p. 103°, and the 5:8-quinone, m.p. 72-73°.

#### POLYMETHYLNAPHTHALENES.

Tetra- and Penta-methylnaphthalenes.—Ruzicka and co-workers obtained 1:2:5:6-tetra-

methylnaphthalene by heating a number of triterpenes and triterpenoid compounds with selenium. In the course of the identification of this compound they synthesised the following and characterised them by their pterates (P) styphnates (S):

- 1:2:5:6-Tetramethylnaphthalene,  
m.p. 116-116.5°.  
P, m.p. 154-154.5°; S, m.p. 160-161°.
- 1:2:6:8-Tetramethylnaphthalene,  
b.p. 166-168°/15 mm.  
P, m.p. 133.5-134°; S, m.p. 135-136°.
- 1:2:5:8-Tetramethylnaphthalene,  
b.p. 150°/9 mm.  
P, m.p. 137-138°.
- 1:2:4:8-Tetramethylnaphthalene,  
b.p. 150°/10 mm.  
P, m.p. 145.5°.
- 1:2:4:5:8-Pentamethylnaphthalene,  
b.p. 150°/10 mm.  
P, 146-147°.
- 1:2:4:6:8-Pentamethylnaphthalene,  
m.p. 106-107°.  
P, m.p. 187-188°.  
(*Helv. Chim. Acta*, 1933, 16, 314).

Methylethyl- and Diethyl-naphthalenes are described in Table VI and call for no special comments. The preparation of 2-methyl-3-ethylnaphthalene from 2-methyl-3-acetyl-5:6:7:8-tetrahydronaphthalene has been patented by Hoffmann-La Roche (Swiss. P.

215656) who use it for obtaining antihæmorrhagic compounds.

The preparation of 2:6-dihydroxy-1:5-diethylnaphthalene, m.p. 262° (dimethyl ether, m.p. 186°), has been described by L. F. Fieser and W. C. Lothrop (J. Amer. Chem. Soc. 1935, 57, 1459) who obtained it by reduction of the 1:5-diacetyl-compound. The compound did not couple with diazo-compounds.

**Dimethylisopropylnaphthalenes, etc.**—Naphthalene hydrocarbons containing methyl and isopropyl groups are the parent substances of plant sesquiterpene compounds found in many essential oils. The most important appears to be *cadalene*, 1:6-dimethyl-4-isopropylnaphthalene, which is formed by dehydrogenation of *cadinene* (v. Vol. II, 188c) with sulphur. *Eudalene*, 1-methyl-7-isopropylnaphthalene, is obtained from *eudesmol* (v. Vol. IV, 393a), a sesquiterpene alcohol found in plants of the eucalyptus family (for references, see Table VII). Besides those given in the Table, a new synthesis of eudalene has since been reported starting from ethyl 6-methylcyclohexane-1-acetate-2-propionate (N. N. Chatterjee and A. Bose, J. Ind. Chem. Soc. 1941, 18, 196), and one of cadalene from ethyl  $\gamma$ -p-tolyl- $\Delta^{\beta}$ -pentenoate (P. C. Dutta, *ibid.* 1941, 18, 233).

A considerable amount of work has been carried out on the preparation of naphthalene derivatives containing higher alkyl groups in the nucleus. R. D. Desai and W. S. Waravdekar (Proc. Indian Acad. Sci. 1941, 13A, 33, 39) condensed  $\alpha$ -naphthol with stearyl chloride by means of zinc chloride in nitrobenzene, obtaining 80% of 2- and 6% of 4-stearyl- $\alpha$ -naphthol. Using  $\alpha$ -methoxynaphthalene and the appropriate acid chloride, substitution took place in the 4-position giving ketones which were reduced to 1-methoxy-4-hexadecyl-, m.p. 224–225°, 4-lauryl-, m.p. 111–112°, and 4-dodecyl-naphthalene, m.p. 165–166°. Y. F. Chi and C. T. Jang (J. Amer. Chem. Soc. 1941, 63, 3155) prepared 2-n-amyl-, m.p. 45–46.5°, 2-isoamyl-, b.p. 135–140°/3 mm., and 2-n-hexyl- $\alpha$ -naphthol, m.p. 42–43°, by a similar method. *n*-Docosylnaphthalene,  $C_{10}H_7 \cdot [CH_2]_{21} \cdot CH_3$ , m.p. 56–58°, and other hydrocarbons have been described by L. A. Mikcska *et al.* (J. Org. Chem. 1941, 6, 787).

Vitamin- $K_1$  has been shown by Doisy and collaborators to be 2-methyl-3-phytyl-[ $\alpha$ ]-naphthoquinone (v. K-VITAMIN, Vol. VII, 87a).

#### NAPHTHYLACETIC ACIDS AND HOMOLOGUES.

$\alpha$ -Naphthylacetic Acid has become of technical interest since the discovery that, like the natural hormone  $\beta$ -indolylacetic acid, it acts as a plant growth stimulant in very small concentrations. It is marketed in preparations for stimulating the rooting of cuttings (see Zimmerman and Wilcoxon, Contr. Boyce Thompson Inst. 1935, 7, 209, and much subsequent literature; also GROWTH-PROMOTING SUBSTANCES, Vol. VI, 138b).

Several methods are available for the preparation of  $\alpha$ -naphthylacetic acid, the most practical being those depending on the hydrolysis of  $\alpha$ -

naphthylacetonitrile, which is prepared by the action of an alkali cyanide on  $\alpha$ -naphthylmethyl chloride or bromide (v. p. 393b). The hydrolysis of the nitrile may be accomplished by boiling with a mixture of dilute sulphuric and acetic acids, the product being precipitated by diluting with a large volume of water. The naphthylacetic acid is purified by dissolving in aqueous ammonia, and fractionally precipitating by addition of acid, the first portion of precipitate being discarded. Further purification is effected by recrystallising first from water, then from benzene (A. Cambron, Canad. J. Res. 1939, 17, B, 10). The nitrile may also be hydrolysed in ether solution by caustic soda (Amer. Cyanamide Co., U.S.P. 2166554). The preparation via  $\alpha$ -naphthylmethyl bromide is described by Olivier and Wit (Rec. trav. chim. 1937, 56, 853). Other patented processes involve the condensation of naphthalene with chloroacetic acid at 165–185° (I.G., G.P. 562391) and the interaction of  $\alpha$ -naphthyl magnesium bromide and chloroacetic acid (U.S.P. 2290401).

$\alpha$ -Naphthylacetic acid crystallises in stout prisms, m.p. 135–135.5° (Olivier and Wit, *l.c.*);  $\alpha$ -naphthylacetonitrile is a colourless oil, b.p. 150–152°/1.5 mm. (Manske and Ledingham, Canad. J. Res. 1939, 17, B, 14).

$\beta$ -Naphthylacetic Acid has m.p. 142°; it is sparingly soluble in water, readily in benzene (Blank, Ber. 1896, 29, 2373; Willgerodt, J. pr. Chem. 1909, [ii], 80, 188). The *amide*, which can be obtained by heating  $\beta$ -naphthyl methyl ketone with ammonium sulphide and sulphur at 220–225°, has m.p. 200°.

A number of  $\alpha$ -naphthyl derivatives of higher fatty acids have been described (Mayer and Sieglitz, Ber. 1922, 55 [B], 1835; Manske and Ledingham, *l.c.*).

#### NAPHTHYL ALKYL KETONES.

Naphthyl alkyl ketones,  $C_{10}H_7 \cdot CO \cdot Alk$ , are formed by the action of acyl chlorides on naphthalene in the presence of aluminium chloride. Substitution takes place not, as might be expected, almost entirely in the  $\alpha$ -position of the naphthalene nucleus, but also to a considerable extent in the  $\beta$ -position, the proportion of  $\alpha$ - to  $\beta$ -isomer formed depending to an important extent on the solvent used and not on temperature. The reaction between naphthalene and acetyl chloride has been studied by several workers. It was stated by E. Caille (Compt. rend. 1911, 153, 393) that acetyl chloride and other acyl chlorides gave only the  $\alpha$ -ketone when the reaction was carried out in carbon disulphide at 0°. Chopin (Bull. Soc. chim. 1924, [iv], 35, 611) confirmed that both in carbon disulphide and in chlorobenzene only the  $\alpha$ -compound was formed; in bromobenzene some  $\beta$ -compound appeared, in ligroin about equal proportions of  $\alpha$ - and  $\beta$ - and in nitrobenzene chiefly  $\beta$ -ketone. N. Fröschl and J. Harlass (Monatsh. 1932, 59, 275) likewise obtained only the  $\alpha$ -compound working in carbon disulphide solution. A. St. Pfau and A. Ofner (Helv. Chim. Acta, 1926, 9, 669), however, obtained  $\alpha$ - and  $\beta$ -isomers in the ratio 65:35 using carbon disulphide, 42:58 in chlorobenzene, and 11:89 in

nitrobenzene. Other workers (private communication) have confirmed the observations of St. Pfau and Ofner. The two isomers are best separated by fractional crystallisation of the picrates from alcohol, the  $\alpha$ -picrate crystallising first. More recently G. Lock (Monatsh. 1942, 74, 77) found that the ketone prepared in carbon disulphide contains not more than 60% of the  $\alpha$ -isomer.

J. W. Williams and J. M. Osborn (J. Amer. Chem. Soc. 1939, 61, 3438) condensed keton instead of acetyl chloride with naphthalene in carbon disulphide in the presence of aluminium chloride and claimed to get mainly the  $\alpha$ -ketone.

Other acyl chlorides give mixtures of  $\alpha$ - and  $\beta$ -ketones with naphthalene in presence of aluminium chloride, e.g. propionyl and *n*-butyryl chloride (G. Bargellini and G. Melacini, Atti. R. Accad. Lincei, 1908, [v], 17, II, 26), oxalyl chloride (C. Liebermann and H. Zsuffa, Ber. 1911, 44, 208), dimethylmalonyl chloride (M. Freund and K. Fleischer, Annalen, 1913, 399, 203), and stearoyl chloride (F. Seidel and O. Engelfried, Ber. 1936, 69 [B], 2573).\*

$\alpha$ -Naphthyl Methyl Ketone is described as an almost odourless liquid, b.p. 300.5–301.5°; St. Pfau and Ofner, and Fröschl and Harlass, by cooling it below 0°, claimed to have obtained it crystalline, m.p. 34°, confirming Claus and Feist (Ber. 1886, 19, 3180), but Lock (*l.c.*) concludes that this was mostly  $\beta$ -compound, and gives the melting-point of the  $\alpha$ -compound 10.5°; its *picrate* has m.p. 118°; *oxime*, m.p. 137–138°. When heated with sulphur it is converted into a thioindigoid dyestuff (Dziewoński *et al.*, Bull. Acad. Polonaise, 1930, A, 198).

$\beta$ -Naphthyl Methyl Ketone has m.p. 54°, b.p. 307.5–308.5°; it has a persistent odour and is said to be used in perfumery; its *picrate* has m.p. 82°; *oxime*, m.p. 145–146°. Heated with sulphur, it gives 2:1-naphththioindigotin.

L. Chopin (Bull. Soc. chim. 1929, [iv], 45, 167) stated that the  $\beta$ -compound undergoes slow spontaneous transformation into the  $\alpha$ -isomer if traces of the latter are present, a most unusual change if the observation is correct.

$\alpha$ -Naphthyl Heptadecyl Ketone has m.p. 54° (H. Ryan and T. Nolan, Proc. Roy. Irish Acad. 1912, B, 30, 1) and the  $\beta$ -ketone m.p. 66–67° (Freund and Fleischer, *l.c.*).

$\alpha$ -Naphthyl Undecyl Ketone is a liquid, b.p. 240–246°/5 mm. (A. W. Ralston and C. W. Christenson, Ind. Eng. Chem. 1937, 29, 194).

$\alpha$ - and  $\beta$ -Naphthyl methyl ketones are convenient starting materials for the preparation of  $\alpha$ - and  $\beta$ -naphthoic acids by oxidation with potassium hypochlorite (L. F. Fieser, H. L. Holmes, and M. S. Newman, J. Amer. Chem. Soc. 1936, 58, 1055).

Hydroxy-derivatives of naphthyl alkyl ketones are formed by the action of acyl chlorides, or the fatty acids, on naphthols in presence of zinc chloride, or by the action of aluminium chloride on naphthyl esters of fatty acids (Fries transformation) or by dealkylating

alkoxynaphthyl alkyl ketones. O. N. Witt and D. Braun obtained 1-hydroxy-2-naphthyl methyl ketone, m.p. 103°, as principal product by the action of acetyl chloride and zinc chloride on  $\alpha$ -naphthol (Ber. 1914, 47, 3216). They showed that the product obtained by Gattermann Ehrhardt and Maisch (*ibid.* 1890, 23, 1209) by the action of acetyl chloride and aluminium chloride on  $\alpha$ -ethoxynaphthalene contains, besides a 52% yield of 4-ethoxy-1-naphthyl methyl ketone, m.p. 78–79°, some 4-hydroxy-1-naphthyl methyl ketone, m.p. 198°, and 2:4-diacetyl-1-naphthol, m.p. 150°. When the 4-ethoxy-1-naphthyl methyl ketone is treated with aluminium chloride it is not only de-ethylated but suffers an isomeric change giving 1-hydroxy-2-naphthyl methyl ketone; in benzene it can be de-ethylated without isomeric change.

The autoxidation of 2-acetyl-1-naphthol in alkaline solution has been studied by K. Fries and H. Leus (*ibid.* 1922, 55 [B], 753).

1-Hydroxy-3-naphthyl methyl ketone, m.p. 167°, was prepared by H. Erdmann (*ibid.* 1888, 21, 635) by distilling benzylidenelacrulic acid.

R. W. Stoughton (J. Amer. Chem. Soc. 1935, 57, 203) heated  $\alpha$ -naphthyl propionate, butyrate, and valerate with aluminium chloride and obtained mainly the 2-acetyl-1-naphthol, with some 4- and some 2:4-diacetyl-1-naphthol (*cf.* Y.-F. Chi, *ibid.* 1939, 61, 2487). 2-Lauryl-, m.p. 74–75° (*Me ether*, m.p. 37–38°), 2-palmityl-, m.p. 83–84° (*Me ether*, m.p. 41–42°), and 2-stearyl-1-naphthol, m.p. 81–82° (*Me ether*, m.p. 42–43°) were obtained by R. D. Desai and W. S. Waravdekar (Proc. Indian Acad. Sci. 1940, 12, A, 507) by heating  $\alpha$ -naphthol with the fatty acid and zinc chloride at 180°.

2-Hydroxy-1-naphthyl methyl ketone (1-acetyl-2-naphthol); m.p. 64°, is obtained when  $\beta$ -naphthyl acetate is treated with aluminium chloride (Fries, Ber. 1921, 54 [B], 709; Fries and Ehlers, *ibid.* 1923, 56 [B], 1305). The Friedel-Crafts reaction with acetyl chloride on  $\beta$ -methoxynaphthalene is influenced by the solvent used, as is the case with naphthalene itself. In benzene or carbon disulphide, the product is 1-acetyl-2-methoxynaphthalene, m.p. 57–58° (not 3-acetyl-2-methoxynaphthalene, as stated by Witt and Braun, *ibid.* 1914, 47, 3224, and disproved by Fries and Schimmelschmidt, *ibid.* 1925, 58 [B], 2835), whilst in cold nitrobenzene, 6-methoxy-2-acetylnaphthalene, m.p. 104–105° is formed in 70% yield.

6-Methoxy-2-propionynaphthalene, m.p. 109°, is similarly prepared (R. D. Haworth and G. Sheldrick, J.C.S. 1934, 864).

3-Acetyl-2-methoxynaphthalene, m.p. 48°, was obtained by Fries and Schimmelschmidt by the action of methyl zinc iodide on 2-methoxy-3-naphthoyl chloride; 3-acetyl-2-naphthol forms yellow leaflets, m.p. 112°, and, unlike the 1:2-isomer, forms alkali salts which are not prone to oxidation in air. With benzaldehyde it condenses to form  $\beta$ -naphthastavone (J. Tambor, G. Plattner, and C. Zäch, Helv. Chim. Acta, 1926, 9, 463). According to Wilson Baker and Carruthers, 3-acetyl-2-naphthol exhibits as much internal chelation as 1:2- and 2:1-isomers (J.C.S. 1937, 479).

1:5-Diacetyl-2:6-dihydroxynaphthalene, m.p.

\* For a comprehensive account of the acylation of naphthalene and derivatives in the presence of aluminium chloride, see C. A. Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publishing Corporation, New York, 1941, pp. 271 *et seq.*



263°, was prepared by L. F. Fieser and W. C. Lothrop (J. Amer. Chem. Soc. 1935, 57, 1463); its dimethyl ether has m.p. 216°, diacetate, m.p. 189°.

### NAPHTHYL ARYL KETONES.

Naphthyl aryl ketones have some technical importance as intermediates for dyestuffs. It was shown by R. Scholl and C. Seer that  $\alpha$ -naphthyl phenyl ketone when heated with aluminium chloride undergoes dehydrogenation and cyclisation to benzanthrone (Annalen, 1912, 394, 111) and this reaction when applied to 1:4- and 1:5-dibenzoylnaphthalenes gives rise to the important vat dyes, the dibenzopyrene-quinones (see ANTHRAQUINONE DYESTUFFS, Vol. I, 426b).

Phenyl  $\alpha$ -Naphthyl Ketone (1-benzoylnaphthalene), m.p. 75.5°, is obtained, together with about 20% of the  $\beta$ -compound, when naphthalene and benzoyl chloride are heated at 180–200° with a small amount of phosphorus pentoxide (H. Lecher, Ber. 1913, 46, 2667), or from naphthalene and benzoic acid, or from  $\alpha$ -naphthoic acid and benzene with phosphorus pentoxide (M. Kollaritz and V. Merz, *ibid.* 1873, 6, 541).

Phenyl  $\beta$ -Naphthyl Ketone, m.p. 82°, is obtained similarly from  $\beta$ -naphthoic acid and benzene. Scholl and Seer (*l.c.*) obtained *o*-tolyl, m.p. 64°, *m*-tolyl, m.p. 74–75°, and *p*-tolyl  $\alpha$ -naphthyl ketone, m.p. 85°, from naphthalene, the respective toluoyl chloride and aluminium chloride in carbon disulphide. They do not consider the possibility of  $\beta$ -isomer being formed.

Phenyl 5:8-Dichloronaphthyl Ketone, from 1:4-dichloronaphthalene and benzoyl chloride in the presence of aluminium chloride, has m.p. 104–105° (I.G., B.P. 301311).

Phthalic anhydride condenses with naphthalene in the presence of aluminium chloride to give a very high yield of *o*- $\alpha$ -naphthoylbenzoic acid, m.p. 176.4°; the conditions for carrying out the reaction have been studied by P. H. Groggins and H. P. Newton (Ind. Eng. Chem. 1930, 22, 157) who recommend using 1.1 mol. of catalyst at 0° in *o*-dichlorobenzene as solvent. If, during the condensation, the temperature is allowed to rise, a substantial amount of *o*- $\beta$ -naphthoylbenzoic acid, m.p. 166°, is formed (E. de B. Barnett and N. C. Campbell, J.C.S. 1935, 1031). When the calcium salt of the  $\alpha$ -acid is heated at 300–330° under reduced pressure it is decarboxylated to give phenyl  $\alpha$ -naphthyl ketone (Scottish Dyes, Ltd., B.P. 289544). The ketone itself when heated with potassium hydroxide at 250–260° decomposes into naphthalene and benzoic acid (L. Olfsen, J. Gen. Chem. Russ. 1939, 9, 36).

Sulphonation of phenyl 1-naphthyl ketone in the cold with 10% oleum gives 1-benzoylnaphthalene-5-sulphonic acid, which is decomposed by heating with 95% sulphuric acid at 160–170° into benzoic acid and naphthalene disulphonic acid (J. S. Joffe and N. N. Melteva, *ibid.*, p. 1104).

1-Benzoylnaphthalene-4-sulphonic acid (chloride, m.p. 117–119°; amide, m.p. 199–200°), is described by Dziewoński and Mosjew (Rocz. Chem. 1931, 11, 169).

By strong chromic acid at 5–10°, phenyl  $\alpha$ -

naphthyl ketone is oxidised in poor yield to 5-benzoyl-[ $\alpha$ ]-naphthaquinone, m.p. 152°, which can be reduced to 5-benzoyl-1:4-dihydroxynaphthalene, m.p. 194–196° (R. Scholl, J. Donat, and S. Hass, Ber. 1935, 68 [B], 2034).

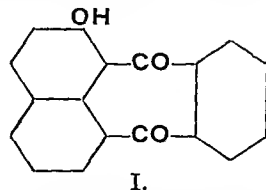
Phenyl 4-hydroxy-1-naphthyl ketone is used under the name of Ciba Naphthol RP (Basle) as a coupling component for the development of azo-dyestuffs on textile fibres (H. Lederer, Textilber. 1931, 12, 461). It has m.p. 164–165° (ethyl ether, m.p. 73°) (cf. Scholl and Seer, Annalen, 1912, 394, 151). A number of patents describe its preparation by condensing  $\alpha$ -naphthol or 1-naphthol-2-carboxylic acid followed by decarboxylation, with benzotrichloride (S.C.I. Basel, B.P. 203824; 212569; 231342). 2:4-Dibenzoyl- $\alpha$ -naphthol has mp. 138–139° (P. E. Popov, J. Gen. Chem. Russ. 1935, 5, 986).

1:5-Dibenzoylnaphthalene, m.p. 186.5°, is the main product when phenyl  $\alpha$ -naphthyl ketone is treated with benzoyl chloride in the presence of aluminium chloride; the 1:8-compound is presumed to be formed at the same time (I.G., B.P. 279506). 1:4-Dibenzoylnaphthalene, m.p. 106°, is obtained by condensing 1-benzoylnaphthalene with benzoyl chloride-aluminium chloride to give 4-benzoyl-1-benzoylnaphthalene, m.p. 110°, and oxidising the benzyl group to benzoyl with nitric acid (I.G., B.P. 333666). Nitro and sulphonyl derivatives of 4-benzoyl-1-benzoylnaphthalene are described by Dziewoński and Mozjew (*l.c.*).

1:8-Dibenzoylnaphthalene, m.p. 189–190° (dioxime, m.p. 270°) was obtained by Dziewoński, Auerbach, and Mozjew (Bull. Acad. Polonaise, 1929, A, 658) by oxidising 8-benzoyl-1-benzoylnaphthalene, m.p. 142°, itself obtained by the action of benzyl chloride on phenyl  $\alpha$ -naphthyl ketone.

2:6-Dibenzoylnaphthalene (dioxime, m.p. 281°) and 2:7-dibenzoylnaphthalene (dioxime, m.p. 176°) have been prepared by oxidation of the corresponding dibenzoylnaphthalenes (Dziewoński and S. Wodolski, Roc. Chem. 1932, 12, 366).

An unusual form of diketone is obtained by the condensation of phthalic anhydride with  $\beta$ -naphthol in concentrated sulphuric acid or using aluminium chloride as condensing agent. It was shown by A. Rieche and E. Frühwald to be 1:8-phthaloyl- $\beta$ -naphthol (I) (Ber. 1931, 64 [B], 1603; 1932, 65 [B], 1371; cf. Fieser, J. Amer.



I.

Chem. Soc. 1931, 53, 3546; 1933, 55, 3342; and for a summary, Annual Rep. Appl. Chem. 1933, 20, 116).

### BENZYL DERIVATIVES OF NAPHTHALENE.

Benzylation of naphthalene with benzyl chloride gives  $\alpha$ -derivatives at lower,  $\beta$ -derivatives at higher temperatures.



$\alpha$ -Benzyl-naphthalene,  $C_{10}H_7 \cdot CH_2Ph$ , m.p.  $59^\circ$  (*picrate*, m.p.  $100-101^\circ$ ), is the main product when naphthalene is heated with benzyl chloride and a small proportion of aluminium chloride for a short time at  $80-90^\circ$ .

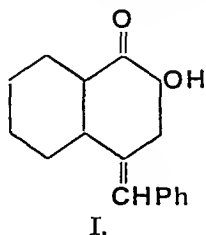
$\beta$ -Benzyl-naphthalene, m.p.  $35-5^\circ$  (*picrate*, m.p.  $93^\circ$ ) is obtained almost exclusively by the same reaction at  $160^\circ$ , adding the aluminium chloride gradually during an hour (L. Roux, Ann. Chim. Phys. 1887, [vi], 12, 289).

For substitution derivatives of  $\alpha$ -benzyl-naphthalene, see Dziewoński *et al.*, Bull. Acad. Polonaise, 1927, A, 273; 1930, A, 66.

According to K. Dziewoński and J. Mozjew, when naphthalene is heated with benzyl chloride at  $100-120^\circ$  in the presence of zinc chloride or aluminium chloride, there are formed, besides monobenzyl-naphthalenes, 1:8-dibenzyl-naphthalene, m.p.  $146-5^\circ$ , " $\beta$ "-dibenzyl-naphthalene, m.p.  $88^\circ$  (*picrate*, m.p.  $107^\circ$ ) and " $\gamma$ "-dibenzyl-naphthalene, m.p.  $132^\circ$ . The 1:8- and " $\gamma$ "-compounds do not form picrates (*ibid.* 1928, A, 283; Roczn. Chem. 1929, 9, 361). The " $\beta$ "-compound was later shown to be 1:4-dibenzyl-naphthalene (Dziewoński *et al.*, Bull. Acad. Polonaise, 1929, A, 650).

2:6-Dibenzyl-naphthalene, m.p.  $91^\circ$ , and 2:7-dibenzyl-naphthalene, m.p.  $123^\circ$ , are formed from naphthalene, benzyl chloride, and aluminium chloride at  $170^\circ$ . By the Friedel-Crafts reaction on 2-benzyl-naphthalene, 6-acetyl-2-benzyl-naphthalene, m.p.  $96^\circ$ , is obtained, from which were prepared 6-acetamido-2-benzyl-naphthalene, m.p.  $189^\circ$ , and 6-amino-2-benzyl-naphthalene, m.p.  $95^\circ$ . 6-Benzoyl-2-benzyl-naphthalene has m.p.  $126-127^\circ$  (Dziewoński and Wodelski, Roczn. Chem. 1932, 12, 366).

1-Benzyl-3:4-naphthaquinone (4-benzyl- $[\beta]$ -naphthaquinone), orange plates, m.p.  $148^\circ$  (decomp.), has been described by L. F. and M. Fieser (J. Amer. Chem. Soc. 1939, 61, 596), according to whom it can exist in the stable tautomeric form, 2-hydroxy-4-benzylidene-1-naphthone (I), yellow needles, m.p.  $182.5-182.8^\circ$ .



1:5-Dibenzyl-2:6-dihydroxynaphthalene, m.p.  $191^\circ$ , was prepared by L. F. Fieser and W. C. Lothrop (*ibid.* 1935, 57, 1463).

E. H. R.

### PART III. HYDROGENATED NAPHTHALENES AND THEIR DERIVATIVES.

#### SYNOPSIS OF THE SUBJECT.

Nomenclature (p. 409d); General Methods for Hydrogenation of Naphthalene (p. 410b); The Action of Metals on Naphthalene (p. 412a); Hydrogenation of Substituted Naphthalenes (p. 412c); Manufacture of Tetralin and Decalin (p. 413c); Uses of Tetralin and Decalin (p. 414a); Isomerism Amongst Hydrogenated Naphthalenes (p. 414c).

Dihydronaphthalenes (p. 415a); Substitution Derivatives (p. 416a).

Tetralin (p. 416d); Tetralin Peroxide (p. 417b); Substitution Reactions (p. 417c); Halogenation (p. 417d); Nitration (p. 418c); Sulphonation (p. 419a); Amino Derivatives (p. 419b); Tetrahydronaphthols (p. 422b); Derivatives of Mixed Aromatic-Aliphatic Character (p. 425c); Alkyl Homologues (p. 426a); Aldehydes (p. 428d); Tetrahydronaphthoic Acids (p. 429a); Tetrahydronaphthalenedicarboxylic Acids (p. 429d); Tetralones (p. 430b); Acyl Derivatives (p. 432b).

Hexahydronaphthalenes (p. 432c).

Octalins (p. 432d).

Decalins (p. 433d); Chlorodecalins (p. 434d); Bromodecalins (p. 435a); Nitrodecalins (p. 435a); Amino and Hydroxy Derivatives (p. 435b); Dihydroxy-decalins (p. 437a); Decahydronaphthaldehyde (p. 437b); Decalin-carboxylic Acids (p. 437b); Decalones (p. 437d); Homologues of Decalin (p. 438c).

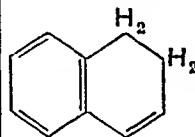
#### Introduction.

Naphthalene being a highly unsaturated hydrocarbon is capable of giving rise to less unsaturated hydrocarbons by addition of hydrogen; its structure shows five double bonds and theoretically each of these can be hydrogenated in turn, giving di-, tetra-, hexa-, octa-, and decahydrides, all of which should show isomeric forms of one kind or another. In fact, hydrocarbons of all these types are known and they and their derivatives have been the subject of a very large amount of chemical work. Two, the tetrahydride, commonly known as tetralin, and the decahydride, decalin, have become of some industrial importance. Of their derivatives and substitution products many have attracted the attention of industrial chemists, but few have found industrial application.

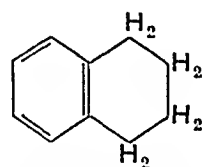
Naphthalene is hydrogenated with greater facility than benzene, an observation in accord with its less truly aromatic character. The course of hydrogenation, however, shows a marked break at the tetralin (1:2:3:4-tetrahydronaphthalene) stage; tetralin shows, in fact, very similar behaviour as regards hydrogenation to a substituted benzene; the intermediate compounds, hexalin and octalin, tend to undergo disproportionation, in presence of catalysts, to tetralin and decalin.

#### Nomenclature.

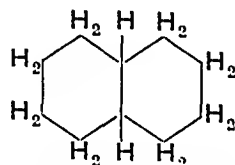
Hydrogenated naphthalenes are correctly named naphthalene hydrides, but it is more usual to call them hydronaphthalenes; numbering is as for naphthalene, thus:



1:2-Dihydronaphthalene.

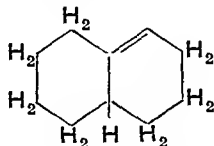


1:2:3:4-tetrahydronaphthalene  
or 5:6:7:8-tetrahydronaphthalene.

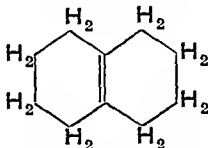


Decahydronaphthalene.

An alternative procedure is to indicate the position of double bonds, this being especially useful with the more highly hydrogenated products such as octahydronaphthalenes, *e.g.*,



$\Delta^1$ -octahydronaphthalene.



$\Delta^9$ -octahydronaphthalene.

The nomenclature proposed by Leroux (Ann. Chim. 1910, [viii], 21, 460) calling decahydronaphthalene "naphthane" and the partially hydrogenated compounds "naphthandiene," "naphthatriene," etc., has not been accepted. The German abbreviations decalin (dekalin), octalin, hexalin, tetralin, are, however, convenient and generally used. The names of functional derivatives are usefully based on these names, *e.g.*, tetralol and decalol for hydroxy derivatives, tetralone and decalone for ketones. Functional derivatives of dihydronaphthalenes and 1:2:3:4-tetrahydronaphthalene are given the prefix *ar-* or *ac-* to indicate that the functional group is in the unhydrogenated or hydrogenated ring, in the former case the compound being *aromatic* and in the latter *alicyclic* in character.

#### General Methods for Hydrogenation of Naphthalene.

Naphthalene can be hydrogenated by many kinds of reducing agent, the most important being (a) hydriodic acid; (b) a metal in combination with an alcohol, water, or other source of hydrogen; (c) hydrogen and a catalyst.

(a) Hydrogenated naphthalenes were obtained by heating naphthalene with hydriodic acid, with or without phosphorus, by Berthelot (Bull. Soc. chim. 1868, [ii], 9, 228), Baeyer (Annalen, 1870, 155, 276), Graebe (Ber. 1872, 5, 678), Agrestini (Gazzetta, 1883, 12, 495), Graebe and Guye (Ber. 1883, 16, 3028), and Wreden (Annalen, 1887, 187, 164). The reaction products are complex and are dependent on the temperature. At temperatures between 170° and 280°, the formation of tetra-, hexa-, and deca-hydronaphthalenes has been reported. There is a suggestion that the tetralin obtained by this process is not identical with the 1:2:3:4-tetrahydronaphthalene obtained by other methods, the supposition being based on the statement by Graebe and Guye that the barium sulphate from their product crystallised with 1.5H<sub>2</sub>O, whilst that from tetralin from other sources is anhydrous (Leroux, *l.c.*) and different in crystalline form.

(b) When naphthalene is reduced by sodium and boiling ethyl alcohol, dihydronaphthalene is

obtained (*v. p.* 415b), but when boiling amyl alcohol is used tetralin is formed (Bamberger and Kitchelt, Ber. 1890, 23, 1561; Leroux, *l.c.*). That the formation of tetralin in the latter case is due to the higher temperature is made probable by the observation that, if naphthalene is heated with sodium in solvent naphtha at 145° and ethyl alcohol added, tetralin is formed (Bayer & Co., G.P. 306724) or water can be used instead of alcohol as a source of hydrogen (Chem. Fabr. Griesheim-Elektron, G.P. 370974). Tetralin is also formed by the action of sodamide (Sachs, Ber. 1906, 39, 3013) or sodium in liquid ammonia (Lebeau and Pichon, Compt. rend. 1914, 158, 1514) on naphthalene. (*See also p. 412a*, action of metals on naphthalene.)

(c) The catalytic hydrogenation of naphthalene results in the formation of tetralin or decalin according to the conditions used. Three kinds of catalyst come into practical consideration; the platinum-palladium type, the nickel type, and the molybdenum oxide or sulphide type, and reaction may be carried out either in the vapour or liquid phase.

The hydrogenation of naphthalene using platinum black as catalyst and ether or glacial acetic acid as solvent was studied by Willstätter and Hatt (Ber. 1912, 45, 1474) and Willstätter and King (*ibid.* 1913, 46, 527), who obtained as sole product decahydronaphthalene, although when 1:2-dihydronaphthalene was treated similarly, tetrahydronaphthalene was formed. Straus and Lemmel also obtained tetralin by hydrogenating 1:2-dihydronaphthalene with palladium as catalyst, but with platinum in glacial acetic acid more highly hydrogenated products were formed (*ibid.* 1921, 54 [B], 25). When it became clear that tetralin was always formed immediately in the hydrogenation of naphthalene to decalin in presence of nickel, Willstätter and Seitz (*ibid.* 1923, 56 [B], 1388) reinvestigated the hydrogenation in presence of platinum black, and discovered that the presence of oxygen was an important factor in determining the course of the hydrogenation. When the catalyst was rich in oxygen, tetralin was formed and was not further hydrogenated; as the amount of oxygen present was decreased, formation of decalin increased and with small amounts of oxygen present only decalin was formed. Further it appeared that with a minimal quantity of oxygen, tetralin is once more the product. These observations led the authors to postulate the primary formation of different dihydro-compounds; the 1:2-compound being the most stable, would be further hydrogenated to tetralin; a dihydro-compound with a hydrogen atom attached to each nucleus might become perhydrogenated if the catalyst were poor in oxygen, or dehydrogenated if it were rich in oxygen.

Zelinsky (*ibid.* 1923, 56 [B], 1723) observed that, in the vapour phase, decalin is smoothly dehydrogenated to naphthalene when passed over palladium black at 300°; tetralin can be hydrogenated to decalin at 120° using the same catalyst, or using platinised asbestos at 150°. R. P. Linstead and his co-workers (J.C.S. 1937, 1146) found that tetralin is quantitatively dehydrogenated by boiling (liquid phase) with

active platinum or palladium, the best form of the latter being palladised charcoal. Decalins (*cis*- and *trans*-) were only very slowly dehydrogenated in the liquid phase, and it is interesting to note that the decalins examined (*trans*- $\Delta^2$  and  $\Delta^9$ ) underwent disproportionation into tetralin and decalin, the former then being dehydrogenated.

The use of a nickel catalyst for the hydrogenation of naphthalene was studied by Ipatieff (Ber. 1907, 40, 1281). He used nickel oxide, and found that, under a pressure of 100–120 atm. at 200–250°, hydrogenation stopped with the formation of tetralin, but when this was retreated with fresh catalyst, decalin, b.p. 189–191°, was formed. Sabatier and Senderens had previously obtained tetralin by passing a mixture of naphthalene vapour and hydrogen over reduced nickel at 200° (Compt. rend. 1901, 132, 1254) and the vapour phase reduction was further studied by Leroix (Ann. Chim. 1910, [viii], 21, 458). He found that hydrogenation to tetralin proceeded readily at 200° using nickel which had been reduced from its oxide at 280°. To hydrogenate the tetralin to decalin, considerable attention to detail is required. A highly active nickel is necessary, the sample used being obtained by reducing the oxide at 250°; and the temperature must be near 160°, since above 170° dehydrogenation of decalin to tetralin occurs. The decalin so obtained had, after purification, b.p. 187–188°. It was also found by Lush (J. Soc. Chem. Ind. 1927, 46, 454*r*) that at 200°, and atmospheric pressure, only tetralin is formed, but as the pressure is increased and reaction takes place more and more in the liquid phase, decalin production increases. At 160°/300 lb. sq. in., the product contained 42.9% of decalin. Similar results were obtained by Kagchira (Bull. Chem. Soc. Japan, 1931, 6, 241) who stated that the decalin obtained at 160°/91 atm. was a mixture of 90% of *cis*- and 10% of *trans*-isomer. The effect of higher temperatures was studied by Watorman, Clausen, and Tulleners (Rec. trav. chim. 1934, 53, 821) using nickel on kieselguhr as catalyst. With an initial pressure of 113 kg./cm.<sup>2</sup> between 243° and 300° only tetralin was formed and no higher hydrogenation occurred. With fresh catalyst, however, hydrogenation could be re-started at 100° and continued up to 257°, giving a mixture of *cis*- and *trans*-decalin. When this mixture was heated with a nickel catalyst at 260–300°, isomerisation occurred, presumably *cis*- changing to *trans*-decalin.

The dehydrogenation of tetralin by Raney nickel has been studied by Adkins and Reid (J. Amer. Chem. Soc. 1941, 63, 741) who found, in the liquid phase, 40% dehydrogenation at 300° and 78% at 350°. These authors prefer to prepare tetralin by hydrogenating naphthalene at 150–200° with a copper chromite catalyst.

When hydrogenation of naphthalene is carried out using a platinum or a nickel catalyst, freedom from catalyst poisons, especially sulphur compounds, is essential, and the naphthalene must first be rigorously purified. The discovery that molybdenum and tungsten oxides and sulphides can be used as hydrogenation catalysts

which are not deleteriously affected by sulphur compounds is therefore of considerable importance. The first patent for this process appears to be that of the Hungarian chemist J. Varga (B.P. 333453; F.P. 683070, 1928) who passed naphthalene over a molybdenum or tungsten catalyst, e.g., molybdic acid, with excess of hydrogen in the presence of hydrogen sulphide or sulphur, at a temperature of 460° using a short contact time (about one minute) and obtained a mixture of tetralin and decalin. M. K. Diakova hydrogenated purified naphthalene to tetralin using molybdenum oxide as catalyst at 435–445°/100–235 atm. (J. Appl. Chem. Russia, 1931, 4, 819). Further work was done in Russia by Prokopetz and Jern (*ibid.* 1934, 7, 159), who state that, using as catalyst molybdenum sulphide 320–370°/200 atm., a mixture of tetralin and decalin is obtained. The decalin formed at 350° is *trans*; any *cis* formed at lower temperatures changes to the *trans*-form in presence of catalyst at 360–370°. At a temperature of 384–390°/100 atm. they obtained 100% conversion of naphthalene into tetralin (Destr. Hydrog. of Fuels, 1934, 1, 275). A patent of I.C.I. and E. D. Kamm (B.P. 401724) states that tungsten sulphide, WS<sub>2</sub>, can be used to hydrogenate naphthalene to tetralin at temperatures between 170° and 300°, and pressures as low as 10 atm.; some hydrogen sulphide is used with the hydrogen to maintain the activity of the catalyst. According to Prokopetz and Pavlenko (Koks i. Chim. 1934, 4, 58) coke-oven gas can be used as the reducing agent with molybdenum sulphide, the best conditions being 420°/250–260 atm. The publications generally agree that molybdenum catalysts require a higher temperature than nickel.

The course of the high-pressure hydrogenation of naphthalene with molybdenum and tungsten catalysts has been discussed in publications by Varga and by Prokopetz which are inaccessible in this country (for summaries see Chem. Zentr. 1935, I, 1642); and by C. C. Hall (Fuel, 1933, 12, 76). There is general agreement that breakdown to benzenoid hydrocarbons starts when a catalyst is present at temperatures above 400°. In the absence of a catalyst Hall found (working in a nickel steel vessel) that naphthalene is stable at 450° but, at 500°, 20–30% is converted into tetralin and low-boiling hydrocarbons. In presence of active carbon and ammonium molybdate tetralin formation starts at 350° and is nearly complete at 400°; at 500°, 50% is converted to low-boiling hydrocarbons, which are supposed to be formed from tetralin in the stages *n*-butylbenzene, ethylbenzene, toluene, benzene. No *o*-xylene was found. These observations agree substantially with those of Ipatieff and Kojukwin using a nickel-alumina catalyst at 450–480°, except that these authors reported formation of *o*-xylene (Ber. 1925, 58 [B], 1). Prokopetz states that decalin is much less thermo-stable than tetralin, beginning to decompose in presence of a molybdenum catalyst at 400°, presumably by dehydrogenation to tetralin. Other observers agree that the benzenoid hydrocarbons arise from decomposition of tetralin, but they differ somewhat as to the products formed. I.G. (B.P.

389171) reported the formation mainly of diethylbenzenes and cymene using molybdenum or tungsten oxides at 340–500°/50–350 atm., whilst Jern, using molybdenum sulphide or tungsten oxide containing sulphur at 415–525°/100 atm., obtained a 70–75% yield of liquid hydrocarbons among which were identified toluene, ethylbenzene, and propylbenzene. Ipatieff (J. Amer. Chem. Soc. 1933, 55, 3696) reported naphthalene along with benzene hydrocarbons under similar conditions, and Kosaka and Dan (J. Soc. Chem. Ind. Japan. 1941, 44, 21b) found cyclopentane, cyclohexane, and methylcyclohexane with benzene derivatives. The last might contain much ethylbenzene (12% yield) under favourable conditions.

### *The Action of Metals on Naphthalene.*

Schlenk and Bergmann have shown (Annalen, 1928, 463, 85; 464, 1) that lithium forms with naphthalene a 1:4-addition compound which is hydrolysed to  $\Delta^2$ -dihydronaphthalene and is converted by carbon dioxide to 1:4-dihydronaphthalene-1:4-dicarboxylic acid, m.p. 226–227°. Sodium reacted very sluggishly with naphthalene, but more recently it has been shown that sodium also reacts with naphthalene in a suitable solvent. Ethyl ether does not favour the reaction, but dimethyl ether, and particularly ethylene glycol dimethyl ether, promote it. Sodium is added in small pieces to a stirred molal solution of naphthalene in the solvent in an atmosphere of nitrogen when a dark green solution is obtained; not more than 1 atomic proportion of sodium can be dissolved per 2 mol. of naphthalene, and the temperature must be kept between –10° and +30° by cooling. When the resulting solution is treated with carbon dioxide, preferably simultaneously with its preparation, a mixture of 1:4-dihydronaphthalene-1:4-dicarboxylic acid, m.p. 228–230° and 1:2-dihydronaphthalene-1:2-dicarboxylic acid, m.p. 185–190°, is formed, about 45–50% yield of the former and 28–32% of the latter (N. D. Scott, J. F. Walker, and V. L. Harsley, J. Amer. Chem. Soc. 1936, 58, 2442; Walker and Scott, *ibid.* 1938, 60, 951; also B.P. 443361; 445417, 449534; U.S.P. 2023793; 2054303; 2060829; 2065756). The 1:4-acid is oxidised by bromine to naphthalene-1:4-dicarboxylic acid and by ferricyanide to  $\alpha$ -naphthoic acid. The 1:2-acid, which is much more soluble in water than the other, is oxidised by ferricyanide to  $\beta$ -naphthoic acid with some  $\alpha$ -isomer (U.S.P. 2054100). The 1:4-acid has been applied to the preparation of resins and plasticisers (U.S.P. 2035346; 2040882; 2060829; 2065756).

The action of potassium on naphthalene in liquid ammonia has been studied by C. B. Wooster and F. B. Smith (J. Amer. Chem. Soc. 1931, 53, 179).

The e are statements that sodium can be used as a catalyst for hydrogenating naphthalene. A process is described in which naphthalene was heated in an autoclave with sodium and hydrogen at 100 atm. pressure and a temperature near 300°; above 300° tetralin was formed and below 300° mainly decalin

(I.G., G.P. 488759). Another patent claims that a lower temperature can be used when the catalyst is a sodium potassium alloy (G.P. 473457). F. W. Bergstrom and J. C. Carson (J. Amer. Chem. Soc. 1941, 63, 2935) describe the hydrogenation of naphthalene to tetralin in the presence of sodium at 172–215°/1,000–2,000 lb. per sq. in. Using lithium as catalyst only a little tetralin was formed; calcium gave 56% conversion to tetralin at 250–265°.

### *Hydrogenation of Substituted Naphthalenes.*

The course of the hydrogenation of substitution derivatives of naphthalene depends on many factors and cannot be foretold from *a priori* considerations. Di- and tetra-hydro-products may be obtained, two possibilities being open, namely hydrogenation of the substituted or of the unsubstituted ring. Under more drastic conditions, decahydro derivatives may be formed. There is also the possibility, frequently realised, of elimination of the substituent group with formation of tetralin or decalin. The course of reduction is governed not only by the nature of the substituent group but also by its position, whether  $\alpha$  or  $\beta$ ; it is also influenced by the nature of the reducing agent, and in the case of catalytic reduction by the activity of the catalyst and by temperature and pressure conditions. A few examples will serve to illustrate these points, especially the hydrogenation of the  $\alpha$ - and  $\beta$ -naphthols and -naphthylamines.

Bamberger and Bordt (Ber. 1890, 23, 215) found that when  $\alpha$ -naphthol is reduced with sodium and amyl alcohol only *ar*-tetrahydro- $\alpha$ -naphthol is formed, and this conclusion was confirmed by Schroeter (Annalen, 1922, 426, 7), who also studied the hydrogenation in presence of a nickel catalyst at 200° and found only 25–30% of *ar*-tetrahydro- $\alpha$ -naphthol in his product, the greater part having been converted into tetralin, though 10% of  $\alpha$ -tetralone was also present. It appeared therefore that the major attack under these conditions was on the ring carrying the hydroxyl group, for the tetralone is an isomerisation product of 3:4-dihydro-1-naphthol, and further hydrogenation of this would give *ac*-tetrahydronaphthol from which tetralin would be formed by dehydration followed by further hydrogenation. Indeed, Brochet and Cornubert, working with a metal catalyst at a lower temperature, 130°, claimed to get a product containing 85% of *ac*- and only 15% of *ar*-tetrahydro- $\alpha$ -naphthol (Bull. Soc. chim. 1922, [iv], 31, 1280). At a still lower temperature (110°) Komatsu and Nodzu obtained 41% of crude *ar*-tetrahydro- $\alpha$ -naphthol and 51% of  $\alpha$ -tetralone with some tetralin, whilst at 135–145° they found only 10% of *ar*- and 90% of mixed *ac*-compound and tetralin (Mem. Coll. Sci. Kyoto, 1923, 6, 177). Kimura (*ibid.* 1931, A, 14, 173) obtained 59.3% of *ac*- and 40.7% of *ar*-tetrahydro- $\alpha$ -naphthol using nickel at 130–150°/63 atm., and stated that the proportion of *ar*-compound increased with increasing pressure of hydrogen. Using a Raney nickel catalyst at 155°. Musser and Adkins (J. Amer. Chem. Soc. 1938, 60, 664) found that

5 parts of *ar*-tetrahydro- $\alpha$ -naphthol were formed against 3 parts of the *ac*-compound, the latter, however, becoming converted to tetralin; using copper chromite as catalyst at 190°, the ratio was 2 parts of *ar*- to 1 part of *ac*-tetrahydro- $\alpha$ -naphthol. Palfray, however, using Raney nickel at 65°/150 kg. per sq. cm., observed the formation of *ac*-tetralol and tetralin only (Compt. rend. 1938, 206, 1976).

$\beta$ -Naphthol, by contrast with  $\alpha$ -naphthol, when reduced with sodium and amyl alcohol, gives predominantly the *ac*-tetrahydro- $\beta$ -naphthol with only a few per cent. of the *ar*-compound (Bamberger and Kitschelt, Ber. 1890, 23, 885; Schroeter, *l.c.*) Using a nickel catalyst, Schroeter again found that the main product was *ac*- $\beta$ -tetralol, and no tetralin or  $\beta$ -tetralone was formed. Brochet and Cornubert (*l.c.*), using a nickel catalyst under pressure at 150°, found 75% of *ac*- and 25% of *ar*-tetralol in their product, absorption of hydrogen stopping at the tetrahydro stage. Musser and Adkins (*l.c.*) obtained 87% yield of the *ac*-tetralol using copper chromite catalyst at 190° (cf. Palfray, *l.c.*). By contrast, it is claimed in B.P. 468375 (I.G.) that when the hydrogenation is carried out in aqueous alkaline or alcoholic alkaline solution, using nickel, nickel-chromium or nickel-cobalt as catalyst,  $\beta$ -naphthol gives only *ar*-tetralol.

The literature on the reduction of naphthol ethers is confused, but it seems fairly clear that, in general,  $\alpha$ -naphthol ethers tend to give *ar*-, and  $\beta$ -naphthol ethers, *ac*-tetralol ethers, whether reduced with sodium and alcohol or with hydrogen and a catalyst (see Musser and Adkins, *l.c.*). It is claimed, however (I.G., B.P. 326762, 1928), that *ar*-compounds only are formed by hydrogenating esters and ethers of  $\alpha$ - and  $\beta$ -naphthol using a nickel catalyst at the comparatively low temperature of 60–70°, the pressure being *ca.* 50 atm.

The two naphthylamines show the same difference in their behaviour on reduction as do the two naphthols. With sodium and amyl alcohol,  $\alpha$ -naphthylamine gives the aromatic base, *ar*-tetrahydro- $\alpha$ -naphthylamine (Bamberger and Althaus e, Ber. 1888, 21, 1786) whilst  $\beta$ -naphthylamine gives a preponderance of *ac*-tetrahydro- $\beta$ -naphthylamine and only a small proportion of aromatic base (Bamberger and Kitschelt, *ibid.* 1890, 23, 876). Catalytic reduction of  $\alpha$ -naphthylamine, *e.g.*, by passing the vapour over reduced nickel at 135–145°, gives mainly (90%) aromatic base, whereas  $\beta$ -naphthol gave mainly *ac*-tetralol (Komatsu and Nodzu, Mem. Coll. Sci., Kyoto, 1923, [A], 6, 177). Similar reduction of  $\beta$ -naphthylamine, however, gives primarily 76% of *ar*- and 24% of *ac*- base, so that with  $\beta$ -naphthylamine the nature of the products is profoundly affected by the reducing agent used (T. Hara, *ibid.* 1924, [A], 7, 406; B.P. 290175; 506928; G.P. 581831). It is stated by the Goodyear Tire Co. (B.P. 395232) that the products of catalytic hydrogenation of *N*-substituted  $\beta$ -naphthylamines are affected by the conditions used; with a nickel catalyst at 180–200°, phenyl- $\beta$ -naphthylamine is said to give almost pure *ac*-tetrahydro derivative (B.P. 418374).

The reduction of other functional derivatives of naphthalene is dealt with under the respective functional derivatives of tetralin.

#### *Manufacture of Tetralin and Decalin.*

The manufacture of tetralin and decalin was started by the Tetralin G.m.b.H. shortly after the end of the war of 1914–1918, using a catalytic process with a nickel-containing catalyst. Very little information regarding the process adopted has been published beyond that contained in a paper by Schroeter (Annalen, 1922, 426, 7). Tetralin and decalin are now manufactured by Imperial Chemical Industries, Ltd.

For the catalytic process, when a catalyst sensitive to sulphur, such as nickel, is to be used, it is essential first to purify the naphthalene. A number of methods for doing this have been patented. According to Schroeter, the crude, hot-pressed naphthalene is treated with finely divided or easily fusible metals and then distilled under reduced pressure. Such methods, using sodium as the metal, are described in G.P. 299012; 299013. The naphthalene may be vaporised and passed over sodium, iron, or nickel at 150°; or the treatment can be carried out in an organic solvent, which may be tetralin. Other methods in which the purifying agent is an absorbing substance such as fuller's earth, kieselguhr, or charcoal, used at 150°, have been described (Tetralin G.m.b.H., G.P. 324861/2/3, 1915–1916), and a metal, nickel or iron, may be used at the same time. A more recently proposed method is to heat crude naphthalene with hydrogen under pressure at 300–470° without any catalyst. The impurities are said to undergo polymerisation and condensation, and by distillation a yield of 80–85% of naphthalene suitable for hydrogenation is obtained (Gewerkschaft M. Stinnes, G.P. 610829). Schroeter (*l.c.*) has described in some detail the laboratory preparation of tetralin (the product obtained had  $\rho^{20}$  0.974–0.976, setting-point  $-27^\circ$  to  $-30^\circ$ , b.p. 206–208°, flash-point 78°), but his description of the manufacturing process is given in very general terms. The manufacturing process worked out by Schroeter, Gewinnor, and Schrauth for the Tetralin G.m.b.H. at Rodleben bei Rossau was based on the laboratory process described by Schroeter.

Decalin was obtained by hydrogenating the tetralin with fresh catalyst under similar conditions at a constant hydrogen pressure of 12–15 atm., the time required being about 4 hours. It can be purified from tetralin and other impurities by digesting with a little sulphuric acid, separating from a resinous residue, washing, drying, and distilling. So obtained it had b.p. 189–191°/770 mm.,  $\rho_4^{18}$  0.8842, and formed a glassy solid at  $-125^\circ$ .

In a modern process the naphthalene to be treated is melted, filtered from solid particles, and pumped to the reaction vessel where it meets the hydrogen and passes with it over the catalyst. The product obtained, which is almost free from naphthalene, is pumped to a still where it is distilled and separated into two main fractions consisting almost exclusively of tetra- and deca-hydronaphthalene respectively. The

separation is good and further purification of the products is not normally necessary.

The British products are marketed under the names "*Tetranap*" and "*Dec*" and conform to the following specifications:

	" <i>Tetranap</i> ."	" <i>Dec</i> ."
Boiling range:		
Not more than 5% below . . . . .	203°	180°
Not less than 95% below . . . . .	208°	195°
Specific gravity at 15°-16°C. . . . .	0.968	0.880
Total sulphur . . . .	0.01%	0.01%
Colour . . . . .	Water-white	Water-white
Flash-point . . . . .	160°F.	126°F.

The British "*Dec*" is almost entirely *trans*-decahydronaphthalene whereas the German Dekalin consists of about 60% *cis*- and 40% *trans*-decahydronaphthalene.

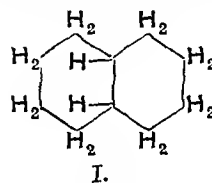
#### Uses of "*Tetranap*" (*Tetralin*) and "*Dec*" (*Decalin*).

Tetralin is a powerful solvent for naphthalene and is used extensively in the gas industry for dissolving naphthalene deposits and, more particularly, for the prevention of such deposits, by the operation of "fogging." This consists in injecting the solvent into the gas stream in the form of a mist or spray. A fall in temperature resulting in naphthalene condensation also causes the simultaneous condensation of sufficient "*Tetranap*" to dissolve the naphthalene and remove it to a collecting vessel. Gum formation is also prevented by "fogging." "*Tetranap*" is also an excellent solvent for meter mechanisms (see F. Schuster, *Gas-u. Wasserfach*. 1930, 73, 1009; P. Deutsch, *ibid.* 74, 245; G. Weissenberger, *ibid.* 1931, 74, 154). "*Tetranap*" has an excellent solvent power for a wide range of oils, waxes, tars, natural and most synthetic resins (Tetralin G.m.b.H., G.P. 301651, 1916). It is miscible in all proportions with aliphatic alcohols (except methanol), with chlorinated hydrocarbons, methylcyclohexane, methylcyclohexanol, methylcyclohexanone, etc. It is used in the paint industry as a paint remover and to prevent or minimise "skinning." It can also be used for the preparation of bitumen emulsions and as a solvent for asphalts and metallic soaps. It is said to be more effective than naphthalene as an insecticide against clothes moth (Colman, *J. Econ. Entomol.*, 1934, 27, 860). It has also been suggested as a dispersion medium in the hydrogenation of coal (Fisher and Eisner, *Ind. Eng. Chem.* 1937, 29, 939). "*Dec*" is a powerful solvent and is sold as a satisfactory substitute for turpentine, finding extensive use in the paint industry. It dissolves drying oils, and although its evaporation rate is low the ultimate drying time of paints and varnishes is unaffected, and the high flash-point diminishes the fire hazard. "*Dec*" dissolves drying oils,

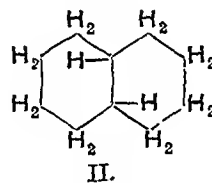
soft resins, natural and synthetic waxes, bituminous materials and, in particular, synthetic resins of the glyptal type. Paints in which "*Dec*" wholly or partially replaces turpentine give a harder and more abrasion-resistant film, and varnish films are less susceptible to wrinkling, silking, and webbing. Paints thinned with "*Dec*" also have superior flow properties.

#### Isomerism Amongst Hydrogenated Naphthalenes.

Only two dihydrides of naphthalene are known, the 1:2- and 1:4-isomers, and only one tetrahydride with certainty, the 1:2:3:4-compound, tetralin. It seems unlikely that other isomers can have any stability. When the 9 and 10 carbon atoms of naphthalene are hydrogenated, *cis-trans* isomerism comes into play; thus decalin exists in two forms, *cis*- and *trans*-, represented diagrammatically in I and II.



*cis*-decalin.



*trans*-decalin.

In the octahydronaphthalene series (octalins), there are four possible positions for the one double bond, namely 1:2, 2:3, 1:9, and 9:10; in addition the first two compounds can show *cis-trans* isomerism, making six isomers in all. The hexalins form a more complicated series, but of these little is known.

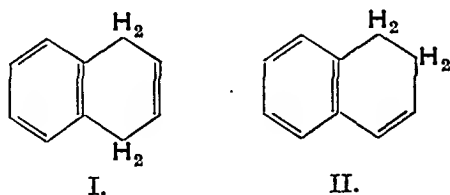
Tetralin forms two series of substituted derivatives, those in which the substituent is in the aromatic nucleus (the *ar*-derivatives) and those in which it is in the hydrogenated ring (the *ac*-series). The former series gives the usual position isomers; in the latter series, mono-substitution products can exist in optically active (*d*- and *l*-) forms, and when more than one carbon atom carries a substituent, *cis-trans* isomerism also appears.

Decalin substitution products are very complicated in their isomerism. The 1- and 2-monosubstitution products can each exist in four forms, two derived from *cis*- and two from *trans*-decalin; in addition, each of these forms is asymmetric and should be resolvable into *d*- and *l*-forms, making eight isomers in all. As the number of substituents increases the number of possible isomers rises rapidly, and the phenomena of isomerism have therefore greatly complicated the study of decalin chemistry.



## DIHYDRONAPHTHALENES.

Two dihydrides of naphthalene are known, namely 1:4-(or  $\Delta^2$ -)dihydronaphthalene (I) and 1:2-(or  $\Delta^1$ -)dihydronaphthalene (II). The



former is the first product of reduction of naphthalene by sodium and ethyl alcohol; the latter is obtained when the former is heated with sodium ethoxide in alcohol. [ $\alpha$ -] and [ $\beta$ -]naphthaquinones are respectively the diketone compounds corresponding with (I) and (II). Both dihydronaphthalenes show the properties of aliphatic ethylene compounds in forming addition compounds with halogens and in forming halohydrins. They do not form picrates.

The heats of hydrogenation of the two dihydronaphthalenes to tetralin, determined by R. B. Williams (J. Amer. Chem. Soc. 1942, 64, 1402) are, for  $\Delta^1$ -dihydro-, -24.6, and for  $\Delta^2$ -dihydronaphthalene, -27.6 kg.-cal. per mol.

The two dihydronaphthalenes are distinguished from one another by their different oxidation products, and their constitutions are thereby confirmed. With potassium permanganate,  $\Delta^2$ -dihydronaphthalene yields *o*-phenylenediacetic acid, whilst  $\Delta^1$ -dihydronaphthalene yields *o*-carboxyphenylpropionic acid (Strauss and Rohrbacher, Ber. 1921, 54 [B], 40), and by the action of ozone and decomposition of the ozonide,  $\beta$ -*o*-aldehydophenylpropaldehyde (von Braun and Zobel, *ibid.* 1923, 56 [B], 2139).

$\Delta^2$ -Dihydronaphthalene (I) is prepared by the method of Bamberger and Lodter (*ibid.* 1887, 20, 3075; Annalen, 1895, 288, 74) by boiling a solution of 15 g. of naphthalene in 300 c.c. of absolute alcohol with 22.5 g. of sodium until the metal has dissolved. The crude product contains besides some naphthalene and tetralin, about 5% of  $\Delta^1$ -dihydronaphthalene (Strauss and Lemmel, Ber. 1921, 54 [B], 25); according to Cook and Hill (J. Amer. Chem. Soc. 1940, 62, 1995) the amount of the last can be reduced to a trace by carrying out the reduction in presence of benzene. The crude product is best purified by preparing the addition compound which  $\Delta^2$ -dihydronaphthalene forms with mercuric acetate, discovered by J. Sand and O. Gennsler (Ber. 1903, 36, 3705) and used for the purpose of separation by Strauss and Lemmel (*ibid.* 1913, 46, 232) and subsequently by other workers. The mercuric acetate compound has m.p. 122° (Sand and Gennsler) and forms a bromide, m.p. 159°. When treated with acid it yields pure  $\Delta^2$ -dihydronaphthalene, m.p. 24.5–25° (Strauss and Lemmel), 25.5° (R. A. Morton and De Gouveia, J.C.S. 1934, 916); b.p. 94.5°/17 mm. (Strauss and Lemmel), 96°/18 mm. (Cook and Hill, *l.c.*);  $\rho_4^{20}$  1.005 (von Auwers, Ber. 1913, 46, 2988). The ultra-violet absorption was studied by Morton and De Gouveia (*l.c.*) who found well-marked bands at

274 and 267 m $\mu$ . and point out that its absorption is practically identical with that of tetralin. According to Kimula and Duniez (Z. physikal. Chem. 1938, 181, 359) both dihydronaphthalenes are dehydrogenated by ultra-violet radiation.

$\Delta^2$ -Dihydronaphthalene has also been obtained by a number of other methods, *e.g.*, from *ar*-5:8-dihydro- $\alpha$ -naphthylamine (Rowe and Levin, J.C.S. 1920, 117, 1577) and by the reduction of *ac*-2:3-dibromotetrahydronaphthalene (Strauss, Ber. 1913, 46, 1051), but none are important for its preparation. The addition compounds are described under tetralin derivatives.

$\Delta^1$ -Dihydronaphthalene (II) is formed quantitatively when  $\Delta^2$ -dihydronaphthalene is heated for 1 hour at 100–105° with 10% sodium ethoxide in alcohol (Strauss, *ibid.* 1913, 46, 1051); the rate of conversion increases with temperature and with the concentration of sodium ethoxide (Strauss and Lemmel, *ibid.* 1921, 54 [B], 25). It was shown by Strauss that the dihydronaphthalene obtained by Willstätter and King (*ibid.* 1913, 46, 527) by distilling *ac*-tetrahydronaphthyltrimethylammonium hydroxide is the  $\Delta^1$ -, not the  $\Delta^2$ -compound as stated. The  $\Delta^1$ -compound has been obtained by a number of other processes, particularly from *ac*-1:2-dibromotetrahydronaphthalene by treatment with zinc and alcohol (Bamberger and Lodter; Strauss and Lemmel; Willstätter and King) or by the action of magnesium and ether, or tin and alcohol (von Braun, G.P. 316218, 1918; von Braun and Kirschbaum, Ber. 1921, 54 [B], 597) or coppered zinc dust (Strauss and Ekhard, Annalen, 1925, 444, 146), or by distilling potassium  $\Delta^1$ -dihydronaphthoate with slaked lime (Strauss and Lemmel); and from *ar*-7:8- or -5:6-dihydro- $\alpha$ -naphthylamine through the diazonium compound (Rowe and Levin, J.C.S. 1920, 117, 1578). It is distinguished from the  $\Delta^2$ -isomer by not forming an additive compound with mercuric acetate, by which it is oxidised to a mixture of stereoisomeric glycols. An account of the addition and oxidation products of  $\Delta^1$ -dihydronaphthalene is given by Strauss and Rohrbacher (Ber. 1921, 54 [B], 40). The dibromide, 1:2-dibromo-1:2:3:4-tetrahydronaphthalene, forms prismatic crystals, m.p. 70–71°.

$\Delta^1$ -Dihydronaphthalene is steam-volatile, has an unpleasant, penetrating smell, and crystallises in plates, m.p. -8 to -7°, b.p. 84–85°/12 mm. (Strauss and Lemmel), m.p. -4°, b.p. 83–84°/5 mm. (Morton and De Gouveia, *l.c.*),  $\rho_4^{20}$  0.997 (von Auwers, *l.c.*). It is difficult to separate by physical means from naphthalene, with which it is said to form an isomorphous mixture. The absorption spectrum has been described by Morton and De Gouveia (*l.c.*) the principal maximum being at 262 m $\mu$ ., with  $\log \epsilon$  4.01.

The oxidation of  $\Delta^1$ -dihydronaphthalene by ozone was studied by von Braun and Zobel (*ibid.* 1923, 56 [B], 2139).

A polymer of  $\Delta^1$ -dihydronaphthalene, m.p. about 220°, has been described by von Braun and Kirschbaum (*l.c.*), and a dimer, m.p. 51–52°, by Walker and Du Pont (U.S.P. 2168011).



# SUBSTITUTION DERIVATIVES OF DIHYDRONAPHTHALENES.

Numerous derivatives of dihydronaphthalenes are recorded in the literature, and only a few can be mentioned here. They are formed, for example, by controlled hydrogenation of substituted naphthalenes, by dehydration of acetralols, and in the course of ring-syntheses of naphthalenic compounds.

1-Bromo- $\Delta^1$ -dihydronaphthalene, b.p. 144–146°/17 mm. was obtained by Strauss and Rohrbacher (*ibid.* 1921, 54 [B], 40) by heating 1:2-dibromotetralin at 130–175° under diminished pressure; von Braun and Kirschbaum (*ibid.*, p. 597) obtained the same compound, b.p. 137°/15 mm., by heating 1:2-dibromotetralin with diethylamine or pyridine.

ar-5:8-Dihydro- $\alpha$ -naphthylamine, or 5-amino- $\Delta^2$ -dihydronaphthalene, colourless plates or needles, m.p. 37.5°, is formed (together with a  $\Delta^1$ -isomer) by reduction of  $\alpha$ -naphthylamine with sodium and absolute ethyl alcohol in the presence of solvent naphtha; it forms a crystalline hydrochloride, an *acetyl* derivative, m.p. 163°, and a *benzylidene* derivative, m.p. 69°. It is converted by heating for 1 hour at 140° with sodium ethoxide into ar-7:8- or -5:6-dihydro- $\alpha$ -naphthylamine, b.p. 180–182°/30 mm., which forms a hydrochloride, feathery needles, an *acetyl* derivative, m.p. 153°, and a *benzylidene* derivative, m.p. 64°, and by elimination of the amino group gives 1:2-dihydronaphthalene (Rowe and Levin, J.C.S. 1920, 117, 1574). The bromination of 5:8-dihydro-acet- $\alpha$ -naphthalide was studied by Rowe and Davies (*ibid.* 1922, 121, 1000).

2-Nitro- $\Delta^1$ -dihydronaphthalene, m.p. 52°, was prepared by Strauss and Ekhard (Annalen, 1925, 444, 146), in a study of the action of nitrous acid on  $\Delta^1$ -dihydronaphthalene.

Reduction of  $\alpha$ -naphthol with sodium and ethyl alcohol in toluene or solvent naphtha gives a mixture of 5:8- and 5:6(or 7:8)-dihydro- $\alpha$ -naphthols. Reduction appears to follow the same course as that of naphthalene, giving first the  $\Delta^2$ -dihydro derivative which is converted by heating with sodium ethoxide to the  $\Delta^1$ -form. If the reduction is completed by distilling off the solvent and heating at 125°, only the  $\Delta^1$ -dihydro derivative is obtained. The latter is reduced by further treatment with sodium and ethyl alcohol to ar-tetrahydro- $\alpha$ -naphthol, whilst ar- $\Delta^2$ -dihydro- $\alpha$ -naphthol is not affected.

ar-5:8-Dihydro- $\alpha$ -naphthol, m.p. 75°, is obtained from the corresponding amine by the diazo reaction. ar-5:6 (or 7:8)-Dihydro- $\alpha$ -naphthol, m.p. 71°, is obtained similarly, or by reduction of  $\alpha$ -naphthol as described above. Both form soluble sulphonic acids which when nitrated, followed by removal of the sulpho-group by hydrolysis, give respectively ar-2-nitro-5:8-, m.p. 98°, and ar-2-nitro-5:6(or 7:8)-dihydro- $\alpha$ -naphthol, m.p. 55° (Rowe and Levin, J.C.S. 1921, 119, 2021). Nitrous acid converts the dihydronaphthols into 4-nitroso-5:8-, m.p. 161°, and 4-nitroso-5:6(or 7:8)-dihydro- $\alpha$ -naphthols (*ibid.* 1927, 531).

Two ac-dihydro- $\alpha$ -naphthoic acids are known. The less stable ac-1:4-dihydro- $\alpha$ -naphthoic acid

is formed when  $\alpha$ -naphthoic acid is reduced with sodium amalgam at low temperatures; it has m.p. 86–87°; *ethyl ester*, b.p. 166–167°/17 mm. The stable 3:4-dihydro-1-naphthoic acid is formed when the labile acid is boiled with sodium hydroxide for some time; it has m.p. 121°; *ethyl ester*, b.p. 185–186°/17 mm. (von Auwers and Möller, J. pr. Chem. 1925, [ii], 109, 124). (For earlier work on these dihydro acids, see Bayer *et al.*, Annalen, 1891, 266, 169; von Sowinski, Ber. 1891, 24, 2354; Kamm and McClugage, J. Amer. Chem. Soc. 1916, 38, 419).

All three ac-dihydro- $\beta$ -naphthoic acids are known. Two are formed in the reduction of  $\beta$ -naphthoic acid by sodium amalgam (Baeyer *et al.*, von Sowinski, *l.c.*; Derick and Kamm, *ibid.* 1916, 38, 400), namely the labile ac-1:2-dihydro-2-naphthoic acid, m.p. 101° (*ethyl ester*, b.p. 152°/12 mm.), and the more stable ac-1:4-dihydro-2-naphthoic acid, m.p. 162–163° (*ethyl ester*, b.p. 163°/12 mm., von Auwers and Möller, *l.c.*). The third most stable isomer is formed by boiling either of the less stable isomers with barium hydroxide under pressure, or with potassium hydroxide. This isomer, ac-3:4-dihydro-2-naphthoic acid, has m.p. 118°, *ethyl ester*, b.p. 159–160°/12 mm. (W. Hüchel and E. Goth, *ibid.* 1924, 57 [B], 1285, give m.p. 120° for the acid). According to von Auwers and Möller, the refractive indices of the ethyl esters of all the above acids are in agreement with the structures assigned to them.

Menthyl esters of the dihydro- $\alpha$ - and - $\beta$ -naphthoic acids have been described by Rupe and co-workers (Annalen, 1903, 327, 188; 1910, 373, 121).

ar-Dihydronaphthoic acids are said to be formed by catalytic hydrogenation of the naphthoic acids in presence of platinum oxide and acetic acid. Thus Ranedo and León (Anal. Fis. Quím. 1927, 25, 421) obtained two isomeric ar-dihydro- $\alpha$ -naphthoic acids from  $\alpha$ -naphthoic acid, one giving an *amide*, m.p. 186°, the other, m.p. 138°, giving an *amide*, m.p. 200°. Similarly León and Charro (*ibid.* 1928, 26, 423) obtained two ar-dihydro- $\beta$ -naphthoic acids, one of m.p. 140–141°, *amide*, m.p. 191°, the other of m.p. 132–133°, *amide*, m.p. 133–134°.

## 1:2:3:4-TETRAHYDRONAPHTHALENE (TETRALIN).

*Physical Properties.*—Tetralin is a colourless, steam volatile oil. Its boiling-point is generally given as 206.5° (Schroeter, Annalen, 1922, 426, 7), but a careful determination by Herz and Schuftan (Z. physikal. Chem. 1922, 101, 269) gave b.p. 207.3°, and m.p.  $-35.0 \pm 0.5^\circ$ . The same authors give the density as  $\rho = 0.9843$  (1–0.000763t); Leroux (Ann. Chim. 1910, [viii], 21, 458) gave  $\rho$  0.984, whilst Schroeter gave  $\rho_{40}^{20}$  0.971; Leuroux gives  $\rho_{40}^{20}$  1.5402. Other constants given by Herz and Schuftan are the vapour pressure, given by  $\log p = -2.6813/T + 1.75 \log T - 0.0032147 + 5.31446$ ; heat of vaporisation, 79.32 cal./g.; Trouton constant 21.8; ebullioscopic constant 5.773; specific heat (15–18°) 0.403; coefficient of expansion (15–25°) 0.0078; critical temperature 789°; surface tension at b.p. 17.46 dynes/cm.; mole-

cular surface energy 512.9. The molecular heat of combustion at constant pressure is 1,341.2/20° (Roth and von Auwers, *Annalen*, 1915, 407, 174). For absorption spectrum, see Morton and De Gouveia, *J.C.S.* 1934, 919; Raman spectrum, Bonino and Cella, *Atti R. Accad. Lincei*, 1931, [vi], 13, 784.

**Chemical Properties.**—The further reduction and destructive hydrogenation of tetralin have already been referred to. When tetralin is distilled with aluminium chloride at 170–270°, the product consists mainly of benzene and its homologues with some cyclopentane and cyclohexane (Turova-Pollak and Lubimova, *J. Gen. Chem. Russ.* 1938, 8, 538); but when it is treated with much less than 1 mol. proportion of aluminium chloride at 100°, the principal products are octahydroanthracene and octahydrophenanthrene, whilst a more prolonged action gives products of higher molecular weight (Tetralin G.m.b.H., G.P. 333158, 1919; Boedtker and Rambech, *Bull. Soc. chim.* 1924, [iv], 35, 631). Schroeter (*Ber.* 1924, 57 [13], 1990) reported the identification of 2:6'-dihydro-*naphthyl* and *α-phenyl-8-naphthyl-n-butane* among the products; the polymerisation of tetralin by aluminium chloride at 50° has also been studied by Waterman and collaborators (*Rec. trav. chim.* 1937, 56, 59).

Oxidation of tetralin takes place by attack on the hydrogenated ring. When alkaline permanganate is used, the product is mainly *o-carboxyphenylpropionic acid*; but by adding finely powdered potassium permanganate to a hot mixture of tetralin and water a nearly quantitative yield of *phthalonic acid* can be obtained (J. von Braun *et al.*, *Ber.* 1923, 56 [B], 2332; G.P. 405459), some *phthalic acid* also being formed. Improved conditions for this reaction are described by W. Davies and H. G. Poole (*J.C.S.* 1928, 1617). By oxidising tetralin with chromic acid in dilute acetic acid, Schroeter obtained 1-ketotetralin (G.P. 346948). By a still milder oxidation, with lead tetra-acetate, R. Criegee obtained 1-acetoxy-1:2:3:4-tetrahydronaphthalene (*Annalen*, 1930, 481, 263).

**Tetralin Peroxide.**—Several workers had early reported that tetralin, especially the technical product, undergoes change on exposure to light and air, and the formation of water by exposing the hot vapour to air had been observed (*cf.* Weger, *Ber.* 1903, 36, 309; Ciamician and Silber, *ibid.* 1913, 46, 421; *Atti R. Accad. Lincei*, 1913, [v], 22, i, 131). In 1932 Hartmann

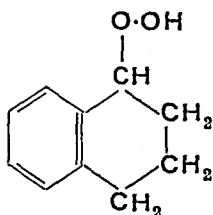
of the substance, m.p. 56° (*cf.* S.C.I. Basle, B.P. 396351), which they prepared by the prolonged passage of air through technical tetralin, at 75°, followed by removal of excess of tetralin under reduced pressure. A similar method of preparation is described by Nussle, Perkins, and Toenies (*Amer. J. Pharm.* 1935, 107, 29) who obtained the pure compound by recrystallising three times from light petroleum—ethyl acetate (70:22). The peroxide liberates iodine from hydrogen iodide, and oxidises leuco-methylene blue. It is stable for a short time at 123° but explodes above this temperature, and also on contact with concentrated sulphuric acid. It can be reduced by zinc dust, or sodium bisulphite in aqueous methyl alcohol to 1-tetralol, and is converted by warm potassium hydroxide into 1-tetralone.

The peroxide may cause distillation residues from tetralin to explode. Antioxidants such as catechol, quinol, and *β-naphthol* inhibit the autoxidation of tetralin (Y. Tanaka *et al.*, *J. Soc. Chem. Ind. Japan*, 1934, 37, 445B; Yamada, *ibid.* 1936, 39, 450B). The kinetics of the autoxidation have been studied by K. Ivanov *et al.* (*Compt. rend. Acad. Sci. U.R.S.S.* 1939, 25, 34) and Medvedev and Podjapol-kaja (*J. Phys. Chem. Russ.* 1939, 13, 717). For a priority claim to the discovery of tetralin peroxide, see H. Kiemstedt (*Brennstoff-Chem.* 1936, 17, 83).

#### SUBSTITUTION REACTIONS OF TETRALIN.

Towards reagents which effect substitution in the aromatic ring, tetralin behaves like a 1:2-substituted benzene, and not like naphthalene. Thus sulphonation occurs mainly in the *β*-position, giving the 6-sulphonic acid; nitration gives a mixture of *α*- and *β*-nitro-compounds; alkylating and acylating agents in the presence of aluminium chloride attack the *β*-position almost, if not quite, exclusively. Phthalic anhydride condenses with tetralin to give *o*-5:6:7:8-tetrahydro-2-naphthoylbenzoic acid, m.p. 153–155° (Schroeter, *Ber.* 1921, 54 [B], 2242); succinic anhydride gives *β*-5:6:7:8-tetrahydro-2-naphthoylpropionic acid, m.p. 121–122° (Kroll-pfeiffer and Schäfer, *ibid.* 1923, 56 [B], 628). The Friedel-Crafts reaction on tetralin has been studied, amongst others, by Scharwin *ibid.* 1902, 35, 2511), Hesse (*ibid.* 1920, 53 [B], 1645), Boedtker and Rambech (*Bull. Soc. chim.* 1924, [iv], 35, 633), and Barbot (*ibid.* 1930, [iv], 47, 1314). For the condensation of tetralin with cyclopentene and cyclohexene, see Pokrovskaja *et al.*, *J. Gen. Chem. Russ.* 1939, 9, 1953, 2291).

**Halogenation.**—Towards halogenating agents tetralin behaves like an alkylbenzene. When it is treated with chlorine or bromine at a low temperature in absence of light, with or without a halogen carrier, substitution takes place in the aromatic ring; at a higher temperature or under illumination the hydrogenated ring is attacked. Chlorination of pure tetralin, cold, in the presence of iron gives a mixture of 1- and 2-chloro-5:6:7:8-tetrahydronaphthalene in the ratio 3:7; both are highly refracting liquids, b.p. about 118–119°/12 mm. By sulphonation they are converted into monosulphonic acids, but the 1-chloro-compound can be sulphonated preferentially leaving the isomer unattacked.



I.

and Seiberth (*Helv. Chim. Acta*, 1932, 15, 1390) reported that tetralin by oxidation with air forms a peroxide to which they gave the formula (I). Hock and Susseml (Ber. 1933, 66 [B], 61) further described the preparation and properties

*ar*-1-*Chlorotetralin*-4-sulphonic acid forms a magnesium salt,  $+2\text{H}_2\text{O}$ , solubility in boiling water 1:40, and sparingly soluble *silver, barium, and lead* salts. *ar*-2-*Chlorotetralin*-3-sulphonic acid forms more soluble salts than the former; the magnesium salt,  $+7\text{H}_2\text{O}$ , has a solubility of 1 part in 5.5 parts of boiling water; the sodium salt,  $+2\text{H}_2\text{O}$ , 1 in 3.

By fusion with caustic alkali the above two acids are converted into *ar*-tetralol sulphonates (Schroeter, Erzberger, and Passavant, Ber. 1938, 71 [B], 1040; cf. G.P. 417927).

According to Green and Rowe (J.C.S. 1918, 113, 970) no *ar*-1-*chlorotetralin* is formed by the action of sodium and amyl alcohol on 1-chloronaphthalene; they obtained it from *ar*-1-aminotetralin by the Sandmeyer reaction and describe it as having an odour similar to that of chlorobenzene; it has b.p.  $250^\circ/748$  mm. By nitration it was converted into *ar*-2:4-*dinitro*-1-*chlorotetralin*, m.p.  $68^\circ$ , in which the chlorine atom is not reactive even to boiling aniline. For the oxidation of *ar*-1-*chlorotetralin*, see von Braun *et al.*, Ber. 1923, 56 [B], 2332.

Exhaustive chlorination of tetralin in diffuse daylight gives 5:6:7:8-*tetrachloro*-1:2:3:4-*tetrahydronaphthalene* (= *ar*-1:2:3:4-*tetrachlorotetralin*), m.p.  $172^\circ$ , b.p.  $180^\circ/26$  mm. (*idem, ibid.*). It forms a *di*bromide, m.p.  $142^\circ$ .

Chlorination of tetralin at  $100^\circ$  yields 1:2-*dischloro*-1:2:3:4-*tetrahydronaphthalene* (*ac*-1:2-*dischlorotetralin*), b.p.  $155$ – $160^\circ/20$  mm., which is difficult to purify (von Braun and Kirschbaum, *ibid.* 1921, 54 [B], 597).

*ac*-2:3-*Dichlorotetralin*, m.p.  $84$ – $85^\circ$ , was obtained by Waser by the action of hypochlorous acid on 1:4-dihydronaphthalene (*ibid.* 1916, 49, 1207). 1:2:3:4-*Tetrachloro*-1:2:3:4-*tetrahydronaphthalene* is naphthalene tetrachloride, obtained by the action of chlorine on naphthalene under mild conditions (see p. 277c). For its crystallography, see J. M. Robertson, Proc. Roy. Soc. 1928, A, 118, 709. Analogous products are obtained by the chlorination of chloronaphthalenes.

*ar*-1-*Bromotetralin*, obtained from 5-amino-1:2:3:4-*tetrahydronaphthalene*, has b.p.  $254$ – $256^\circ/758$  mm. (Smith, J.C.S. 1904, 85, 728); *ar*-2-*bromotetralin* has been obtained in a similar manner (Morgan, Mickelthwait, and Winfield, *ibid.*, p. 736). All the homonuclear mononitro derivatives of *ar*-1 and -2-*bromotetralins*, and also *ar*-1-*bromo*-2:4-*dinitro*- m.p.  $93$ – $94^\circ$ , and 2-*bromo*-1:3-*dinitro*-*tetralin*, m.p.  $135$ – $136^\circ$ , have been described by Veselý and Chudozilov (Bull. Soc. chim. 1925, [iv], 37, 1436).

Bromination of tetralin at about  $100^\circ$  gives *ac*-1:2-*disbromotetralin*, m.p.  $70^\circ$  (von Braun and Kirschbaum, Ber. 1921, 54 [B], 597; G.P. 316218), the same compound as that obtained by addition of bromine to  $\Delta^1$ -dihydronaphthalene. Whether this is the *cis*- or *trans*-compound or a mixture does not appear to be known. The  $\alpha$ -bromine is readily replaced by hydroxyl or alkoxy. The isomeric *ac*-2:3-*disbromotetralin*, m.p.  $71$ – $72^\circ$ , is obtained by addition of bromine to  $\Delta^2$ -dihydronaphthalene (Straus and Lemmel, *ibid.* 1913, 46, 232). This compound differs from the 1:2-*disbromo*-compound in that only the latter develops acid when boiled with

methyl alcohol. The 2:3-*disbromo*-compound is converted into naphthalene with loss of hydrogen bromide by heat, concentrated sulphuric acid, or alcoholic potash.

*ar*-1-*Iodotetralin*, b.p.  $150^\circ/17$  mm.,  $279$ – $280^\circ/765$  mm., is obtained from the corresponding amine by the diazo-reaction (Lesslie and Turner, J.C.S. 1932, 281). The following nitro derivatives have been described: *ar*-1-*iodo*-3-*nitro*-, m.p.  $118$ – $118.5^\circ$ , *ar*-2-*iodo*-1-*nitro*-, m.p.  $84^\circ$ ; *ar*-2-*iodo*-3-*nitro*-, m.p.  $76$ – $76.5^\circ$ ; and *ar*-3-*iodo*-1-*nitro*-*tetralin*, m.p.  $64$ – $65^\circ$  (Cumming and Howie, *ibid.* 1931, 3176).

Nitration.—Nitro derivatives of tetralin can be obtained by nitration if care is taken to prevent oxidation and resinification. Schroeter *et al.* (Annalen, 1922, 426, 39; cf. B.P. 148923, 1920) carried out the operation by using a mixed acid containing rather more than the usual amount of sulphuric acid and water, adding the mixed acid to the tetralin at not above  $0^\circ$ . Thus, a mixture of 120 g. of nitric acid,  $\rho$  1.35, and 260 g. of sulphuric acid,  $\rho$  1.84, is added drop by drop to 132 g. of well stirred and cooled tetralin, and stirring is continued for half an hour after the acid has all been added. Separation of the nitro-compounds from the acid is effected by adding 200–300 c.c. of carbon tetrachloride in which they dissolve. The carbon tetrachloride layer is separated, washed with very dilute caustic soda solution, dried with calcium chloride, and fractionally distilled. The nitrotetralin distils at  $163$ – $175^\circ/13$  mm.; yield 80% of theory.

The product so obtained consists of a mixture of about equal amounts of 5- and 6-*nitro*-1:2:3:4-*tetrahydronaphthalene* (*ar*-1- and -2-*nitro*-*tetralins*), which are separated by fractional distillation under reduced pressure followed by crystallisation, by cooling of the enriched fractions and recrystallisation from methyl alcohol. 1-Nitrotetralin can also be obtained by partial hydrogenation (nickel catalyst) of the mixture, the 2-nitro-compound being preferentially reduced. According to Veselý and Chudozilov (Rec. trav. chim. 1925, 44, 352) the 2-nitro-compound is preferentially reduced by sodium hydrosulphide, but the 1-nitro-compound by sodium monosulphide, especially when the mixture contains a greater proportion of the 2-nitro-compound.

*ar*-1-*Nitrotetralin* has m.p.  $34^\circ$ , b.p.  $157^\circ/13$  mm.,  $\rho^{40^\circ}$  1.1757.

*ar*-2-*Nitrotetralin*, m.p.  $31.5^\circ$ , b.p.  $169^\circ/13$  mm.,  $\rho^{40^\circ}$  1.1762.

The nitrotetralins can be dehydrogenated practically quantitatively to nitronaphthalenes by treating with bromine at  $100^\circ$  and heating at a higher temperature, when hydrogen bromide is evolved (von Braun, Hahn, and Seemann, Ber. 1922, 55 [B], 1687; Tetralin G.m.b.H., G.P. 332593, 1919). The oxidation of the nitrotetralins by permanganate has been studied by von Braun *et al.* (Ber. 1923, 56 [B], 2332).

Dinitration of tetralin gives a mixture consisting for the most part of *ar*-1:3- and 1:2-*dinitrotetralins* which when crystallised from glacial acetic acid form a eutectic, needles, m.p.  $72$ – $73^\circ$ , separable by crystallisation from sulphuric acid into *ar*-1:2-*dinitrotetralin*, m.p.  $102$ – $103^\circ$ , and *ar*-1:3-*dinitrotetralin*, m.p.  $95^\circ$ . Further

nitration of the 1:2-dinitro-compound gives *ar*-1:2:4-*trinitrotetralin*, m.p. 94.5–95°, which forms with 1:3-dinitrotetralin a eutectic mixture, m.p. 82–83°.

*ar*-1-*Nitrotetralin-3-sulphonic acid* is obtained by sulphonating 1-nitrotetralin with 10% oleum at 70–80°; the *amide* has m.p. 189°. This acid is formed together with an isomeric acid, presumably 2-nitrotetralin-4-sulphonic acid (*amide*, m.p. 211–212°), when the total nitration product of tetralin is sulphonated. Sodium 2-nitrotetralin-4-sulphonate is less soluble in water than the isomeric salt (Schroeter *et al.*, *Annalen*, 1922, 426, 139).

**Sulphonation.**—Tetralin is readily sulphonated, even more readily than naphthalene, by concentrated sulphuric acid and by chlorosulphonic acid; when the former acid is used the main product is *ar*-tetralin-2-sulphonic acid; sulphonation with excess of cold chlorosulphonic acid gives a mixture of about equal amounts of the 1- and 2-sulphonyl chlorides (Schroeter *et al.*, *l.c.*, p. 84).

*ar*-Tetralin-1-sulphonic acid can be separated from the 2-sulphonic acid by crystallisation from chloroform, in which the latter acid is more soluble; from this solvent it crystallises with  $\text{H}_2\text{O}$ , m.p. 105–110°; from water it crystallises with  $2\text{H}_2\text{O}$ ; the sodium salt crystallises with  $2\text{H}_2\text{O}$ ; ammonium salt, anhydrous; barium salt,  $3\text{H}_2\text{O}$ ; lead salt,  $3\text{H}_2\text{O}$ ; sulphonyl chloride, m.p. 70–72°; *amide*, m.p. 139–140°; *anilide*, m.p. 148–149°. The sulphonyl fluoride, m.p. 75–77°, has been prepared from tetralin and fluorosulphonic acid (Steinkop, *J. pr. Chem.* 1927, [ii], 117, 53).

*ar*-Tetralin-2-sulphonic acid crystallises from sulphuric acid with  $2\text{H}_2\text{O}$ , m.p. 75°; sodium salt,  $\text{H}_2\text{O}$ ; ammonium and barium salts, anhydrous; lead salt,  $\text{H}_2\text{O}$ ; sulphonyl chloride, m.p. 58°; *amide*, m.p. 135–137°; *anilide*, m.p. 155–156°.

Reduction of the tetralin-1- and -2-sulphonyl chlorides to sulphinic acids and finally to the 1- and 2-thiols, the condensation of these with chloroacetic acid to form thiolacetic acids and the conversion of these into thioindigo dyestuffs has been described by Schroeter (*l.c.*; see also G.P. 299604, 1916; 336615, 1919; B.P. 148419). *ar*-Tetralin-1-sulphinic acid was also prepared by Morgan, Micklethwait, and Winfield (*J.C.S.* 1904, 85, 736), from the sulphonic acid, which they obtained from *ar*-1-aminotetralin-4-sulphonic acid.

*ar*-Tetralin-1:3-disulphonic acid (*disulphonyl chloride*, m.p. 103–104°) is obtained when the 2-sulphonic acid is heated for 10 hours at 160° with 25% oleum. When fused with alkali it loses the  $\beta$ -sulphonic acid group as sulphuric acid, giving *ar*-tetrahydro-*a*-naphthol (Schroeter, *Ber.* 1938, 71 [B], 1053).

#### AMINO DERIVATIVES OF TETRALIN.

Reference has already been made to the difference in behaviour of  $\alpha$ - and  $\beta$ -naphthylamines on reduction (p. 413b).

*ar*-Tetrahydro-*a*-naphthylamine. — This base is the principal product when  $\alpha$ -naphthylamine is reduced by sodium and amyl alcohol, or by sodium and ethyl alcohol if a high boiling

solvent such as solvent naphtha is used, the alcohol being added to the mixture of solvent, sodium, and naphthalene at, say, 145° (*F. Bayer and Co.*, G.P. 305347; 306724; Rowe, *J. Soc. Dyers and Co.* 1919, 35, 130; *J.S.C.I.* 1920, 39, 241r); water may, under such conditions, be used instead of alcohol (*Chem. Fabr. Griesheim-Elektron*, G.P. 370974). Schroeter (*Annalen*, 1922, 426, 23) obtained the base by hydrogenation of *ar*-1-nitrotetralin, or of the mixed 1- and 2-nitrotetralins, the amines being separated by crystallisation of the hydrochlorides from water, or of the methanedisulphonates from 90% alcohol, or by a method of preferential acetylation.

According to Lindner and Siegel (*Monatsh.* 1925, 46, 225) the nitrotetralins are best reduced to amines by iron and alcohol in presence of calcium chloride.

*ar*-Tetrahydro-*a*-naphthylamine is a colourless oil, darkening on exposure to air, b.p. 146°/12 mm. (Schroeter, *l.c.*); 275°/712 mm. (Banberger and Althausse, *Ber.* 1888, 21, 1786). The acetyl derivative has m.p. 158°, benzoyl derivative, 154° (Lindner and Siegel, *l.c.*), benzylidene derivative, m.p. 61.5° (Rowe and Levin, *J.C.S.* 1920, 117, 1579). Urea and thiourea derivatives of *ar*-tetrahydro-*a*-naphthylamine were described by Banberger and Althausse (*l.c.*).

*ar*-Tetrahydro-*a*-naphthylamine hydrochloride forms double salts with mercuric chloride,  $\text{B}, \text{HCl}, \text{HgCl}_2$ , m.p. 179–180°;  $2(\text{B}, \text{HCl})\text{HgCl}_2$ , m.p. 217.5–219°;  $\text{B}, \text{HCl}, 2\text{HgCl}_2$ , m.p. 192.5–193.5° (Grohmann and Brouwer, *Annalen*, 1909, 365, 50).

Intermediate compounds formed by reduction of *ar*-1-nitrotetralin including azoxy, azo-, and hydrazino-compounds have been described by Schroeter (*l.c.*), and also the application of the benzidine conversion to hydrazotetrahydro-naphthalene (*cf.* B.P. 170867, 1920; G.P. 333157, 1916). *ar*-Tetrahydro-*a*-naphthylamine forms a normal diazo-compound from which azo-dyes have been prepared.

Oxidation of *ar*-tetrahydro-*a*-naphthylamine with permanganate gives, not phthalic acid but adipic and oxalic acids; with dichromate and sulphuric acid, tetrahydronaphthaquinone is formed (*q.v.*).

**Derivatives.** — *ar*-4-Bromotetrahydro-*a*-naphthylamine, m.p. 42°, is formed by bromination of acyl derivatives of the base in glacial acetic acid, followed by hydrolysis; the acetyl derivative has m.p. 180–181°, formyl, m.p. 164.5°, propionyl, m.p. 185–186°, benzoyl, m.p. 202–203° (Morgan *et al.*, *J.C.S.* 1904, 85, 736). For other bromo derivatives, see Rowe and Davies *ibid.* 1922, 121, 1000).

*ar*-Tetrahydro-1-naphthylamine-4-sulphonic acid was obtained by Schroeter (*l.c.*) by sulphonating the base with concentrated sulphuric acid, or 10% oleum; according to later work (*I.G.*, G.P. 629653) the product of sulphonation with sulphuric acid at 80–90°, or with chlorosulphonic acid in tetrachloroethane at 135°, consists of 40% of the 2- and 60% of the 4-sulphonic acid.

Nitro derivatives of *ar*-tetrahydro-*a*-naphthylamine are obtained by nitrating the acetyl

derivative with mixed nitric-sulphuric acids followed by hydrolysis. The main product is the 4-nitro-derivative, but Schroeter (l.c.) also isolated the 2- and 3-nitro-compounds (cf. Green and Rowe, J.C.S. 1918, 113, 959).

ar-2-Nitrotetrahydro- $\alpha$ -naphthylamine, m.p. 87–88°, *acetyl*, 184–185°.

ar-3-Nitrotetrahydro- $\alpha$ -naphthylamine, m.p. 78°, *acetyl*, 193°.

ar-4-Nitrotetrahydro- $\alpha$ -naphthylamine, m.p. 116°, *acetyl*, 178°.

ar-2:4-Dinitrotetrahydro- $\alpha$ -naphthylamine has m.p. 181°, *acetyl* derivative 202° (Green and Rowe), or 204° (Schroeter).

N-Methyl-ar-tetrahydro- $\alpha$ -naphthylamine has b.p. 150–152°/12 mm., *picrate*, m.p. 174° (von Braun *et al.*, l.c.).

N-Ethyl-ar-tetrahydro- $\alpha$ -naphthylamine is formed by reduction of ethyl- $\alpha$ -naphthylamine with sodium and alcohol (Bamberger and Helwig, Ber. 1889, 22, 1311) or by hydrogenation with a nickel catalyst (S.C.I. Basle, B.P. 276571). It is an oil, b.p. 286–287°/717 mm.; *acetyl* derivative, m.p. 159–160°. It forms an oily N-nitroso-compound which changes in acid alcoholic solution to the 4-nitroso-compound, m.p. 119°.

Dimethyl-ar-tetrahydro- $\alpha$ -naphthylamine, b.p. 261–262°/721 mm., has been obtained both by reduction of dimethyl- $\alpha$ -naphthylamine (Bamberger and Helwig, l.c.) and by methylation of ar-tetrahydro- $\alpha$ -naphthylamine (Morgan and Richards, J.S.C.I. 1905, 24, 652). It forms a *methiodide*, m.p. 164–5°, more readily than does dimethyl-o-toluidine and, according to von Braun, Arkuszewski and Köhler (Ber. 1918, 51, 282) reacts slowly with formaldehyde in concentrated hydrochloric acid to give a 4-hydroxy-methyl derivative, the *picrate* of which has m.p. 92–94°.

N-Phenyl-ar-tetrahydro- $\alpha$ -naphthylamine has m.p. 43–5°, b.p. 198°/8 mm. (S.C.I. Basle, B.P. 276571).

ar-Tetrahydro- $\beta$ -naphthylamine (5:6:7:8-tetrahydro-2-naphthylamine) is only formed to the extent of 3–4% by sodium-amyl alcohol reduction of  $\beta$ -naphthylamine, but to a greater extent by catalytic reduction (see p. 413b; cf. Lindner *et al.*, Monatsh. 1923, 44, 337). It is prepared by the reduction of ar-tetrahydro- $\beta$ -nitronaphthalene or by reduction of the nitro-compound of tetralin and separation of the bases as described by Schroeter (l.c.). According to the I.G. (G.P. 434403) the mixed amines obtained by this reduction can be separated by treatment with formaldehyde in hydrochloric acid solution, when the  $\alpha$ -compound forms a diarylmethane derivative and the  $\beta$ -compound is left unchanged. The I.G. claim that the mixture of ar- (75%) and ac- (25%) tetrahydro- $\beta$ -naphthylamines obtained by catalytic reduction of  $\beta$ -naphthylamine can be separated by crystallisation of the ar-base from ligroin (G.P. 581831).

The  $\beta$ -base has also been obtained from the oxime of ar-tetrahydro- $\beta$ -naphthyl methyl ketone by the Beckmann change (Scharwin, Ber. 1902, 35, 2511) and from ar-tetrahydro- $\beta$ -naphthoamide (von Braun, Kirschbaum, and

Schuhmann, *ibid.* 1920, 53, 1161); it has m.p. 38–5–39–5° (G.P. 581831 gives m.p. 48°) b.p. 275–277°/713 mm., 147–149°/13 mm., and its odour resembles that of aniline (*acetyl* derivative, m.p. 107°; *benzoyl*, m.p. 166–167°; *phthalamic acid*, m.p. 156–158–5°; *phthalimide*, m.p. 169–171°). The *hydrochloride* and *sulphate* of the base are sparingly soluble in cold water and one-sixth as soluble as the  $\alpha$ -compound in alcohol. When oxidised with alkaline permanganate it gives, like the  $\alpha$ -compound, *adipic acid* (Bamberger and Kitschelt, Ber. 1890, 23, 876). For the application of the Skraup reaction to the base, see von Braun and Gruber (*ibid.* 1922, 55 [B], 1710), and of the quinaldine synthesis, Lindner *et al.* (l.c.).

*Derivatives.*—In nuclear substitution reactions ar-tetrahydro- $\beta$ -naphthylamine resembles a substituted aniline, the 1-position not having the special reactivity which it has in  $\beta$ -naphthylamine. In the Doebner-Miller quinaldine synthesis the amine gives a mixture of both possible tetrahydro- $\beta$ -naphthaquinaldines (Lindner and Stauer, Monatsh. 1925, 46, 231).

Bromination of ar-tetrahydroacet- $\beta$ -naphthalide in glacial acetic acid gives a mixture of 1- and 4-bromo derivatives in the ratio 7:1, the latter being the more soluble in acetic acid. ar-1-Bromotetrahydro- $\beta$ -naphthylamine has m.p. 52–5 (*acetyl*, m.p. 125–5); ar-4-bromotetrahydro- $\beta$ -naphthylamine has m.p. 52° (*acetyl*, m.p. 151°); only the former is steam-volatile (Smith, J.C.S. 1904, 85, 728).

Nitration of ar-tetrahydroacet- $\beta$ -naphthalide follows a different course. In acetic acid the major product is the 3-nitro derivative, with 1-nitro in smaller amount. In sulphuric acid the main product is the 4-nitro, with a smaller quantity of 3-nitro- and little, if any, 1-nitro derivative (Schroeter, Annalen, 1922, 426, 26). The melting-points of the nitroaminotetralins so obtained are:

ar-1-nitro-2-aminotetralin, m.p. 96°, *acetyl*, 126–127°.

ar-3-nitro-2-aminotetralin, m.p. 125–127°, *acetyl*, 132–134°.

ar-4-nitro-2-aminotetralin, m.p. 55°, *acetyl*, 194–195°.

ar-Tetrahydro-2-naphthylamine-4-sulphonic acid was obtained by Schroeter by catalytic reduction of the corresponding nitro-compound (p. 419a); it forms a sparingly soluble crystalline powder; the sodium salt is readily soluble in water. Sulphonation of ar-tetrahydro- $\beta$ -naphthylamine gives ar-2-aminotetralin-3-sulphonic acid (I.G., G.P. 629653).

The following ar-dinitrotetrahydro- $\beta$ -naphthylamines have been described (Schroeter, l.c.):

ar-1:3-Dinitrotetrahydro- $\beta$ -naphthylamine, m.p. 166–168°; its *acetyl* derivative, m.p. 189–191°, is obtained by further nitration of ar-1- or -3-nitrotetrahydroacet- $\beta$ -naphthalide, in sulphuric acid solution.

ar-3:4-Dinitrotetrahydro- $\beta$ -naphthylamine, m.p. 157°; its *acetyl* derivative, m.p. 175–177°, is the main product of dinitration of ar-tetrahydro-aceto- $\beta$ -naphthalide in sulphuric acid, and of its 4-nitro derivative.

N-Methyl-*ar-tetrahydro-β-naphthylamine* has been obtained in the form of its *acetyl* derivative, m.p. 67–69°, by methylating the sodio derivative of *ar-tetrahydroacet-β-naphthalide*, and as an oil, b.p. 267.5°/210 mm. by reducing methylene-*ar-tetrahydro-β-naphthylamine* with sodium in amyl alcohol (Smith, J.C.S. 1904, 85, 732). N-Dimethyl-*ar-tetrahydro-β-naphthylamine*, b.p. 287°/718 mm., is the main product of reducing N-dimethyl-β-naphthylamine with sodium and amyl alcohol (Bamberger and Müller, Ber. 1889, 22, 1295).

N-Ethyl-*ar-tetrahydro-β-naphthylamine* is formed to the extent of 4%, the main product being the alicyclic base, when N-ethyl-β-naphthylamine is reduced with sodium and amyl alcohol. The base, which is steam-volatile, has b.p. 291.5°/720 mm.; *hydrochloride*, m.p. 173.5°; nitrosamine, an oil (Bamberger and Müller, l.c.).

N-Diethyl-*ar-tetrahydro-β-naphthylamine*, b.p. 167°/16 mm., 298°/709 mm., is formed, with the alicyclic isomer, by reduction of N-diethyl-β-naphthylamine with sodium and amyl alcohol; it does not react with formaldehyde to give a 1:1'-methylene-compound (Morgan, J.C.S. 1900, 77, 819).

N-Phenyl-*ar-tetrahydro-β-naphthylamine* has m.p. 65–66°, *hydrochloride*, m.p. 147–148° (Goodyear Tire and Rubber Co., B.P. 418374, 1933).

#### *ar-Di- and Tri-aminotetrahydronaphthalenes.*

*ar-Diamines* derived from tetralin have been obtained by reduction of naphthylenediamines, or of dinitro-, nitroamino-, and nitro-azo derivatives of tetralin.

*ar-Tetrahydro-1:2-naphthylenediamine*, has m.p. 84–85°, b.p. 172–175°/13 mm., (Schroeter); 1-*acetyl* derivative, m.p. 149–151°; di-*acetyl* derivative, m.p. 245°; di-*hydrochloride*, m.p. 260° (decomp.). It is formed by reduction with sodium and amyl alcohol of 1:2-naphthylenediamine in 15% yield, along with the alicyclic isomer (Bamberger and Schieffelin, Ber. 1889, 22, 1374), and by reduction (catalytic or stannous chloride) of 1:2-dinitrotetralin (Schroeter) It forms a *phenanthrazine*, m.p. 228.5–230°.

*ar-Tetrahydro-1:3-naphthylenediamine*, m.p. 84–85° or 89° (1-*acetyl* derivative, m.p. 173°; 3-*acetyl* derivative, m.p. 110–111°; di-*acetyl* derivative, m.p. 245–246°) is obtained by reduction of *ar-1:3-dinitrotetralin* (Schroeter, l.c., p. 78; G.P. 333157, 1916).

*ar-Tetrahydro-1:4-naphthylenediamine*, m.p. 83–85°, b.p. 203°/18 mm.; mono-*acetyl* derivative, m.p. 156°, di-*acetyl* derivative, m.p. 291–292° (Schroeter), is the sole product of reduction of 1:4-naphthylenediamine with sodium and alcohol (Bamberger and Schieffelin, l.c.), and is also obtained by reduction of *ar-1-nitro-4-aminotetralin* (Green and Rowe, l.c.).

*ar-Tetrahydro-2:3-naphthylenediamine*, m.p. 135–136°, was obtained by Schroeter, l.c.) by reduction of the 2-nitro-3-amine. With boiling acetic acid it forms *ar-2-methyl-2:3-tetrahydronaphthiminazole*, m.p. 251–250°, and with phenanthraquinone an *azine*, m.p. 214–216°.

*ar-1:2:3-Triaminotetralin* forms a tri-*acetyl* derivative, m.p. 285°, and *ar-1:2:4-*

*triaminotetralin* a tri-*acetyl* derivative, m.p. 315°; both bases are unstable in air (Schroeter, l.c., p. 81).

#### *ar-Tetrahydronaphthylamines as Dyestuff Intermediates.*

There are numerous references in the literature to the use of *ar-tetrahydronaphthylamines* in the production of azo-dyes, but such dyes have not found technical application. *ar-Tetrahydro-α-naphthylamine* couples with diazo-compounds forming azo-dyes resembling in shade those obtained from benzenoid amines rather than those from α-naphthylamine; *ar-tetrahydro-β-naphthylamine* does not form azo-compounds with diazotised amines, but diazo-amino-compounds (Smith, J.C.S. 1902, 81, 900); the same is true of 4-substituted tetrahydro-α-naphthylamines (Morgan, Micklethwaite, and Winfield, *ibid.* 1904, 85, 743). The properties of dyestuffs derived from diazotised tetrahydro-α-naphthylamines have been described by Rowe (J. Soc. Dyers and Col. 1919, 35, 128; 1925, 41, 5).

*ac-Tetrahydro-α-naphthylamine* is a strongly basic compound, forming a viscid oil, b.p. 246.5°/714 mm. It is formed in very small amount when α-naphthylamine is reduced with sodium and alcohol, and is best obtained by reduction of the oxime of 1-ketotetrahydronaphthalene with sodium and alcohol (von Braun, Braunsdorf, and Kirschbaum, Ber. 1922, 55 [B], 3648). Bamberger and Bammann prepared it by oxidising 1-amino-5-hydrazino-1:2:3:4-tetrahydronaphthalene with copper sulphate (*ibid.* 1889, 22, 951). It forms a stable *nitrite*, m.p. 138–139°, not decomposed by boiling water, and an *acetyl* derivative, m.p. 148–149°.

*ac-Tetrahydro-β-naphthylamine*, a very strong base, is the principal product when β-naphthylamine is reduced with sodium and amyl alcohol (Bamberger and Müller, *ibid.* 1888, 21, 847; Bamberger and Kirschelt, *ibid.* 1890, 23, 876). Its preparation, using sodium and isopropyl alcohol, is described in detail in Organic Syntheses, Coll. Vol. I, p. 846. The base is purified by precipitation as carbonate from ether solution. The pure base is a viscid liquid of pyridine-like odour, b.p. 118.5°/8 mm. 249.5°/710 mm.,  $d_4^{20}$  1.031. It forms an *acetyl* derivative, m.p. 107.5°, and *benzoyl* derivative, m.p. 150–151°. Many salts and other derivatives have been described; with benzene diazonium chloride it forms an explosive diazoamino-compound. The pure *nitrite* of the base has m.p. 137° (Noyes and Ballard, Ber. 1894, 27, 1450). Physiologically, the base has a powerful mydriatic action, also shown by its N-ethyl and dimethyl derivatives, but not by the corresponding *ac-tetrahydro-α-naphthylamine* (Bamberger and Fiehe, *ibid.* 1889, 22, 777).

The following N-alkyl derivatives of *ac-tetrahydro-β-naphthylamine* have been described.

N-Methyl-*ac-tetrahydro-β-naphthylamine*, mobile oil, b.p. 118–119.8°/9 mm.,  $d_4^{20}$  1.024; *hydrochloride*, sinters 196°, m.p. 214°; *platini-*



chloride, m.p. 228°; it was obtained by methylating *ac*-tetrahydro- $\beta$ -naphthylamine with dimethyl sulphate (Waser, *ibid.* 1916, 40, 1202).

N - *Dimethyl-ac-tetrahydro- $\beta$ -naphthylamine*, b.p. 132.3–133.1°/11 mm. (Waser), 116°/22 mm. (Bamberger and Müller, *ibid.* 1889, 22, 1295); *hydrochloride*, m.p. 214–215° (decomp.); *platini-chloride*, m.p. 210° (decomp.). Its *methiodide*, m.p. 228°, is formed by exhaustive methylation of *ac*-tetrahydro- $\beta$ -naphthylamine. The dimethyl base is formed when its methochloride is distilled (Waser) and in small amount, together with the *ar*-isomer, by reduction of N-dimethyl- $\beta$ -naphthylamine with sodium and alcohol (Bamberger and Müller).

N - *Ethyl-ac-tetrahydro- $\beta$ -naphthylamine*, b.p. 267°/724 mm., 153°/23 mm.; *hydrochloride*, m.p. 223.5°, *nitrate*, m.p. 184°; *nitrite*, m.p. 180°; *picrate*, m.p. 183.4°; for other salts and derivatives, see Waser (*l.c.*), and Bamberger (*l.c.*). It is a strong base resembling *ac*-tetrahydro- $\beta$ -naphthylamine, and is formed in 35–40% yield, with the *ar*-isomer, by reduction of N-ethyl- $\beta$ -naphthylamine with sodium and amyl alcohol.

N - *Diethyl-ac-tetrahydro- $\beta$ -naphthylamine* is obtained in very low yield by reduction of N-diethyl- $\beta$ -naphthylamine with sodium and amyl alcohol (Bamberger and Williamson, *ibid.* 1889, 22, 1760), the main product being the *ar*-isomer.

N - *Phenyl-ac-tetrahydro- $\beta$ -naphthylamine*, b.p. 175–180°/2–3 mm., *hydrochloride*, m.p. 238–240°, is the main product of hydrogenating N-phenyl- $\beta$ -naphthylamine with a nickel catalyst, and can be used as a rubber antioxidant (Goodyear Tire and Rubber Co., B.P. 418374, 1933).

#### TETRAHYDRONAPHTHOLS.

The course of hydrogenation of  $\alpha$ - and  $\beta$ -naphthols to the *ar*- and *ac*-tetrahydro derivatives has already been discussed. The individual compounds and some of their derivatives will now be described.

*ar*-Tetrahydro- $\alpha$ -naphthol (5:6:7:8-*Tetrahydro-1-naphthol*, *ar-1-tetralol*) is a white, crystalline solid, m.p. 68.5–69°, b.p. 264.5–265.5°/705 mm., 147°/14 mm. It can be obtained as already described by reduction or hydrogenation of  $\alpha$ -naphthol (p. 412d); from *ar*-tetrahydro- $\alpha$ -naphthylamine (Bamberger and Althausse, Ber. 1888, 21, 1893). According to Schroeter it was manufactured by the Tetralin G.m.b.H. by fusing sodium 5:6:7:8-tetrahydro-naphthalene-1-sulphonate with caustic potash at 220–280°, the yield being 80% of theory (Annalen, 1922, 426, 7). The same author has also described its preparation from *ar*-1-chloro-tetralin-4-sulphonic acid (p. 418a) and from *ar*-tetralin-1:3-disulphonic acid (p. 419b).

Ethers and esters of *ar*-tetrahydro- $\alpha$ -naphthol are obtained by catalytic hydrogenation of the ethers and esters of  $\alpha$ -naphthol (I.G., B.P. 326762, 1928; Musser and Adkins, J. Amer. Chem. Soc. 1938, 60, 664). The *methyl* ether is a liquid, b.p. 113°/7 mm.; *ethyl* ether, b.p. 122°/9 mm.; *acetate*, m.p. 73–75°; *benzoate*, m.p. 46°; *carbonate*, m.p. 114°.

*Derivatives.* — *ar*-*Tetrahydro- $\alpha$ -naphthol-4-sulphonic acid* is formed by the action of cold concentrated sulphuric acid on *ar*-1-tetralol (Green

and Rowe, J.C.S. 1918, 113, 967) or by alkaline hydrolysis of *ar*-1-chlorotetralin-4-sulphonate in the presence of copper (Schroeter *et al.*, Ber. 1938, 71 [B], 1048). It forms a sodium salt +1H<sub>2</sub>O; *barium* salt, +3H<sub>2</sub>O.

Nitration of the 4-sulphonic acid gives *ar*-2-nitrotetrahydro-1-naphthol-4-sulphonic acid, yellow, m.p. 182°.

*ar*-2-Nitrotetrahydro-1-naphthol, yellow, steam volatile, m.p. 56°, is obtained by hydrolysis of the above sulphonic acid with dilute sulphuric acid; further nitration gives *ar*-2:4-dinitrotetrahydro-1-naphthol, m.p. 105° (Green and Rowe, *l.c.*).

*ar*-4-Nitrotetrahydro-1-naphthol, m.p. 123°, is obtained by oxidising *ar*-4-nitrosotetrahydro-1-naphthol, m.p. 163°, formed by the action of nitrous acid on *ar*- $\alpha$ -tetralol, with dilute nitric acid (Rowe and Levin, J.C.S. 1927, 530).

*ar*-Tetrahydro- $\alpha$ -naphthol couples with diazobenzene in the 4-position, to give 4-benzeneazo-*ar*-tetrahydro- $\alpha$ -naphthol, m.p. 144–145°, identical with the phenylhydrazone of tetrahydro-[ $\alpha$ ]naphthaquinone (Rowe and Levin, *l.c.*). The semidine transformation of its *ethyl* ether, m.p. 91.5°, on reduction, has been studied by Jacobson and Turnbull (Ber. 1898, 31, 890).

*ar*-2-Aminotetrahydro- $\alpha$ -naphthol, obtained by reduction of the nitro-compound, and from the 2-bromo-compound (Tetralin G.m.b.H., G.P. 335476), has m.p. 110–111°.

*ar*-3-Aminotetrahydro- $\alpha$ -naphthol, m.p. 197°, *acetyl*, m.p. 211°, was obtained by Schroeter *et al.* (Annalen, 1922, 426, 157) from *ar*-1-amino-3-acetamidotetralin.

*ar*-4-Aminotetrahydro- $\alpha$ -naphthol, m.p. 146–147°, was obtained by reduction of the 4-nitroso-compound and of the 4-*p*-sulphobenzeneazo derivative. Its *ethyl* ether has m.p. 60° and gives a urea, *ar*-4-ethoxy-1-tetralylcarbamide, m.p. 240–241° which does not possess a sweet taste (Schroeter *et al.*, *l.c.*, p. 155).

By the action of carbon dioxide under pressure, alkali salts of *ar*-1-tetralol are converted into salts of *ar*-tetrahydro-1-naphthol-2-carboxylic acid, m.p. 165–166°, *acetyl* derivative, m.p. 170°; *methyl* ester, m.p. 56° (Schroeter *et al.*, *l.c.*, p. 158; F. Bayer and Co., G.P. 335602).

*ar*-Tetrahydro- $\beta$ -naphthol (5:6:7:8-*Tetrahydro-2-naphthol*, *ar-2-tetralol*). Since the main product of reduction of  $\beta$ -naphthol is the alcohol, *ac*-tetrahydro- $\beta$ -naphthol, the *ar*-compound is best prepared by another method. Schroeter (Annalen, 1922, 426, 119; cf. B.P. 148408, 1920) recommends the fusion of *ar*-tetralin-2-sulphonic acid with 75% caustic alkali at 280° for 2½–3 hours. The phenol is precipitated by carbon dioxide from the aqueous solution of the alkali salt, followed by distillation with superheated steam under reduced pressure. It is best recrystallised from light petroleum, when it forms lustrous needles, m.p. 61.5–62.5°, b.p. 148°/12 mm. Nishimatsu and Kimura record having observed two forms (A, 1928, 285). It has a faint creosote odour and possesses phenolic properties, including bactericidal action.

There are patents for the catalytic hydrogenation of ethers and esters of  $\beta$ -naphthol (Chem. Fabr. Griesheim-Elektron, G.P. 370974;



I.G., B.P. 326762, 1928), but according to Musser and Adkins the tetrahydro-products are alicyclic. The acetate of *ar*- $\beta$ -tetralol is a viscous oil, b.p. 158°/14 mm.; the benzoate has m.p. 96°. The 4-nitrobenzoate, m.p. 106.5°, cinnamate, m.p. 77.5°, carbonate, m.p. 111°, and ethyl ether, b.p. 129°/11 mm., are described by Thoms and Kross (Arch. Pharm. 1927, 265, 336). For esters of *ar*-tetralol having chemotherapeutic properties, see Chem. Fabr. von. F. Heyden A.-G., G.P. 414261, 1922; 457060, 1925. For the ultra-violet absorption of *ar*- $\alpha$ - and  $\beta$ -tetralol, see Komastsu, Masumoto, and Kumamoto (Mem. Coll. Sci. Kyoto, 1924, [A], 7, 287).

**Derivatives.**—*ar*-1-Bromo-2-tetralol, m.p. 74°, is obtained by direct bromination of *ar*-2-tetralol; further bromination gives *ar*-1:3-dibromo-2-tetralol, m.p. 37°, also obtained by bromination of the 3-sulphonic acid or the 1-bromo-3-sulphonic acid; its acetate has m.p. 87°.

Sulphonation of *ar*-2-tetralol gives the 3-sulphonic acid, which forms a sparingly soluble sodium salt; bromination of this, or sulphonation of *ar*-1-bromo-2-tetralol, gives *ar*-1-bromo-2-tetralol-3-sulphonic acid (Schroeter, Annalen, 1922, 426, 122; cf. Ber. 1938, 71 [B], 1040). Sulphonation of *ar*-2-methoxytetralin, an oil, b.p. 129–131°, gives the 3-sulphonic acid, m.p. 107°.

Nitration of *ar*-2-tetralol with nitric-sulphuric acid gives the 1:3-dinitro derivative, but with nitrogen peroxide in tetranitromethane, *ar*-3-nitro-2-tetralol, m.p. 88–89°, is obtained (Thoms and Kross, *l.c.*). 1-Bromo-3-nitro-2-tetralol, m.p. 129°, is obtained by nitrating *ar*-1-bromo-2-tetralol-3-sulphonic acid. 1-Chloro-3-nitro-2-tetralol has m.p. 96°. *ar*-1:3-Dinitro-2-tetralol is prepared by dissolving *ar*-2-tetralol in concentrated sulphuric acid (the 3-sulphonic acid being formed), diluting, cooling, and adding nitric acid,  $\rho$  1.4. It forms yellow needles, m.p. 141°, and explodes when heated above its melting-point. The sodium and potassium salt both explode violently at 180–190° but the ammonium, barium, and lead salts do not (Schroeter, *l.c.*, p. 142). The methyl ether has m.p. 86.5°.

*ar*-1-Amino-2-tetralol, m.p. 148°, was obtained by Schroeter (*l.c.*, p. 99) by reduction of *ar*-1-benzeneazo-2-tetralol, and also by demethylating its methyl ether, m.p. 64°, which was obtained by reduction of 1-amino-2-methoxynaphthalene with sodium and amyl alcohol. The aminotetralol forms a cyclic urethane, m.p. 189–190°.

*ar*-3-Amino-2-tetralol, m.p. 202°, was obtained by Schroeter from 1-bromo-3-amino-2-tetralol, m.p. 127°, which was prepared by reduction of 1-bromo-3-nitro-2-tetralol (*v. supra*). The cyclic urethane has m.p. 196°.

*ar*-4-Amino-2-tetralol, m.p. 177°, is obtained via its acetyl derivative, m.p. 222°, from 4-acetamidotetrahydro- $\beta$ -naphthylamine.

By reduction of *ar*-1:3-dinitro-2-tetralol, Schroeter obtained 1-nitro-3-amino-2-tetralol, copper-coloured needles, m.p. 127°, and 1:3-diamino-2-tetralol, colourless leaflets, m.p. 214–216° (decomp.) (*l.c.*). *ar*-1-Nitro-3-amino-2-methoxytetralin has m.p. 117°.

For heteronuclear aminotetralols, see p. 425c.

*ar*-2-Tetralol can be carboxylated directly by heating in the form of alkali-metal derivative

with carbon dioxide under pressure. According to Tetralin G.m.b.H. (G.P. 357663) the potassium derivative is heated at 160° for 5–6 hours with carbon dioxide under 10 atm. pressure. The product, according to Schroeter, is 2-hydroxy-5:6:7:8-tetrahydronaphthalene-3-carboxylic acid, white needles, m.p. 177–178°, and this constitution has been confirmed by Robinson and Walker (J.C.S. 1935, 1531). The methyl ester has m.p. 42°; ethyl ester, b.p. 179°/13 mm.; azide, m.p. 99–100°; anilide, m.p. 182–184°. The I.G. state that 2:3-hydroxynaphthoic acid and anilido can both be hydrogenated catalytically to the *ar*-2-tetralol-3-carboxylic acid and anilide respectively (B.P. 468375), and according to Arnold, Zaugg, and Sprung (J. Amer. Chem. Soc. 1941, 63, 1314), ethyl 2:3-hydroxynaphthoate can be similarly hydrogenated in the presence of Raney nickel to give a 94% yield of ethyl *ar*-2-tetralol-3-carboxylate, b.p. 155–161°/4 mm. They give the melting-point of the free acid as 180–182°. *ar*-2-Methoxytetralin-3-carboxylic acid has m.p. 113–114°.

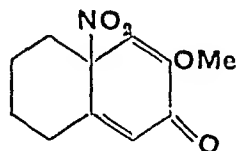
*ar*-1-Nitro-2-tetralol-3-carboxylic acid forms yellow needles, m.p. 200–202°; it is reduced by hydrogen-nickel to 1-amino-2-tetralol-3-carboxylic acid, m.p. 208–210°; diacetyl derivative, m.p. 180–181° (Schroeter, *l.c.*).

*ar*-2-Tetralol-1-carboxylic acid, m.p. 174–176°, was obtained by Arnold, Zaugg, and Sprung (*l.c.*) by oxidation of the corresponding aldehyde; the methoxy acid has m.p. 148–150°.

*ar*-Dihydroxytetralins, etc. — 1:2-Dihydroxy-5:6:7:8-tetrahydronaphthalene has m.p. 69–70° (diacetate, m.p. 96–97°); it is obtained by desulphonation of the 3-sulphonic acid. *ar*-1:3-Dihydroxytetralin, obtained by acid hydrolysis of the 1:3-diamino at 270–290°, has m.p. 122° (diacetate, m.p. 39–40°; dimethyl ether, m.p. 38.5–39.5°) (Schroeter *et al.*, Ber. 1938, 71 [B], 1040).

*ar*-1:4-Dihydroxytetralin, m.p. 185°, is obtained by catalytic reduction of 5:8-dihydroxy-1:4-dihydronaphthalene, and its diacetate, m.p. 186–187°, by hydrogenation of the corresponding diacetate. *ar*-1:2:4-Triacetoxytetralin, has m.p. 142–143° (Diels, Alder, and Stein, *ibid.*, 1929, 62 [B], 2337).

*ar*-2:3-Dimethoxytetralin, m.p. 53°, when nitrated forms a compound, m.p. 92–93° (decomp.), to which the annexed formula has been assigned.



By treatment with boiling alcohol followed by methylation it gives *ar*-1-nitro-2:3-dimethoxytetralin, m.p. 88–89° (Lewis and R. Robinson, J.C.S. 1934, 1253).

*ac*-Tetrahydro- $\alpha$ -naphthol (1-hydroxy-1:2:3:4-tetrahydronaphthaleno), an oil, b.p. 132–134°/12–13 mm.,  $\rho_4^{17}$  1.0986,  $n_D^{17}$  1.5671, can be obtained by reducing *ac*-1-kototetralin with sodium and absolute alcohol or sodium and moist ether. Its phenylurethane, m.p. 121–122°,

decomposes when heated, giving  $\Delta^1$ -dihydronaphthalene (Straus and Lemmel, Ber. 1921, 54 [B], 25).

ac-Tetrahydro- $\beta$ -naphthol is a colourless, viscid oil with an odour of sage, b.p.  $264^\circ/716$  mm.,  $144.5-145.6^\circ/20$  mm.,  $\rho_4^{17}$  1.0715,  $n_D^{17}$  1.5523; phenylurethane, m.p.  $99^\circ$ . It has the character of an alcohol, is insoluble in alkali, but forms a sodium derivative with sodium in ether. The phenylurethane, chloride, iodide, and acetate (fruity odour, b.p.  $169^\circ/34$  mm.,  $268-280^\circ/\text{atm.}$ ) all tend to decompose when heated, giving  $\Delta^1$ -dihydronaphthalene (Bamberger and Lodter, *ibid.* 1890, 23, 197; Straus and Rohrbacher, *l.c.*). ac-2-Methoxytetralin, b.p.  $123-124^\circ/16$  mm., has been obtained by hydrogenating 2-methoxy-3,4-dihydronaphthalene in the presence of palladium.

Many derivatives of ac-tetralols have been obtained from the two isomeric dihydronaphthalenes by taking advantage of their property of forming addition compounds at the reactive double bond of the partially hydrogenated ring, for example with bromine and with hypochlorous acid and hypobromous acid, etc. Pioneer work in this field was carried out by Bamberger and Lodter on  $\Delta^2$ -dihydronaphthalene (*ibid.* 1893, 26, 1833; Annalen, 1895, 288, 74) and by Straus and Rohrbacher on  $\Delta^1$ -dihydronaphthalene (Ber. 1921, 54 [B], 40), and other workers have contributed. The following short summary indicates the compounds thus obtained.

ac-2-Chloro-1-hydroxytetralin, m.p.  $92^\circ$ , is obtained by the action of hypochlorous acid on  $\Delta^1$ -dihydronaphthalene. The corresponding ac-2-bromo-1-hydroxytetralin, m.p.  $111-112^\circ$ , is obtained by the action of water on ac-1,2-dibromotetralin, in which only the bromine in position 1 is active; treatment of the latter with methyl alcohol gives 2-bromo-1-methoxytetralin, a liquid, b.p.  $159^\circ/17$  mm. (Tetralin G.m.b.H., G.P. 335477, 1919). ac-2-Iodo-1-hydroxytetralin has been prepared by Tiffeneau and Orékhoff, who state that, when oxidised with silver nitrate in ether, it is converted into *hydrindene-2-aldehyde* (Compt. rend. 1920, 170, 465).

Several ethers and esters of 2-bromo-1-hydroxytetralin have been described and these by the action of ammonia, primary or secondary amines are converted into derivatives of ac-2-amino-1-hydroxytetralin which are said to have useful physiological, including hypnotic, properties (see Straus and Rohrbacher, *l.c.*). Some of the compounds which have been described are given in the following table (cf. Tetralin G.m.b.H., G.P. 335476/7, 1919; von Braun and Kirschbaum, Ber. 1921, 54 [B], 597; 1922, 55, 3648; von Braun and Weissbach, *ibid.* 1930, 63 [B], 3052):

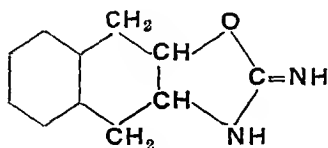
ac-2-amino-1-hydroxytetralin	m.p. $112^\circ$ .
ac-2-methylamino-1-hydroxytetralin	b.p. $164-166^\circ/12-13$ mm.
ac-2-dimethylamino-1-hydroxytetralin	b.p. $157-158^\circ/10$ mm.
ac-2-diethylamino-1-hydroxytetralin	b.p. $170^\circ/10$ mm.
ac-2-piperidino-1-hydroxytetralin	m.p. $72-73^\circ$ .
ac-2-dimethylamino-1-methoxytetralin	b.p. $147-149^\circ/13$ mm.
ac-2-methylamino-1-methoxytetralin	b.p. $144-146^\circ/14$ mm.

ac-2-piperidino-1-methoxytetralin	b.p. $191-193^\circ/15$ mm.
ac-2-dimethylamino-1-ethoxytetralin	b.p. $152^\circ/13$ mm.
ac-2-piperidino-1-ethoxytetralin	b.p. $170^\circ/11$ mm.

A series of compounds isomeric with the above is obtained from  $\Delta^2$ -dihydronaphthalene. By the action of hypochlorous acid on this hydrocarbon its chlorohydrin is obtained, i.e., ac-2-chloro-3-hydroxytetralin, which forms silky needles, m.p.  $117.5^\circ$ , and sublimes at  $100^\circ$ ; it is steam-volatile (Bamberger and Lodter, *l.c.*; E. S. Cook and A. J. Hill, J. Amer. Chem. Soc. 1940, 62, 1995). Its reaction with alkalis is complicated; the products differ according to the conditions used, and include  $\Delta^2$ -dihydronaphthalene-2:3-oxide, ac-dihydro- $\beta$ -naphthol, dihydronaphthalene-2:3- and -1:3-glycols,  $\beta$ -tetralone, naphthalene, and  $\beta$ -naphthol. The acetate of the chlorohydrin has m.p.  $47^\circ$ , benzoate, m.p.  $64-65^\circ$ .

ac-2-Bromo-3-hydroxytetralin, m.p.  $112^\circ$ , is obtained by the action of hypobromous acid on  $\Delta^2$ -dihydronaphthalene (Leroux, Ann. Chim. 1910, [viii], 21, 458; Gonzalez and Campoy, Anal. Fis. Quím. 1922, 20, 534), and a compound, m.p.  $106-165^\circ$ , by the addition of hydrogen bromide to the 2:3-oxide (Bamberger and Lodter, *l.c.*). The iodohydrin has m.p.  $120^\circ$ .

By the action of primary or secondary amines on ac-2-chloro-3-hydroxytetralin, or on the corresponding 2:3-oxide, derivatives of ac-2-amino-3-hydroxytetralin are obtained. ac-2-Amino-3-hydroxytetralin was obtained by Bamberger, Lodter, and Deicke (Annalen, 1895, 288, 116) from the product of the reaction of the chlorohydrin with phthalimide and subsequent removal of phthalic acid by hydrolysis; their product was an oil, giving a hydrochloride, m.p.  $265^\circ$ : Takeda and Kuroda (J. Pharm. Soc. Japan, 1921, 1), however, describe it as a solid, m.p.  $107-108^\circ$ ; hydrochloride, m.p.  $215^\circ$ ; they obtained it via the 2-imidooxazolidine, m.p.  $158-159^\circ$ ,



obtained by heating 2:3-dibromotetralin with carbamide. There is a good deal of discrepancy amongst the physical constants recorded by different authors for members of this series of compounds:

2-Hydroxy-3-methylaminotetralin, m.p.  $85^\circ$ ; hydrochloride, m.p.  $214^\circ$  (Takeda and Kuroda); -3-dimethylamino-, oil; hydrochloride, m.p.  $224^\circ$  (Takeda and Kuroda); b.p.  $183^\circ/27$  mm., hydrochloride, m.p.  $180-181^\circ$  (Bamberger, Lodter, and Deicke); -3-diethylamino-; b.p.  $202^\circ/38$  mm., hydrochloride, m.p.  $167-170^\circ$  (Bamberger, Lodter, and Deicke); hydrochloride, m.p.  $168-170^\circ$  (Cook and Hill); -3-dibutylamino-, b.p.  $155-7^\circ/3$  mm. (Cook and Hill); -3-piperidino-, m.p.  $46-48^\circ$  (Bamberger, Lodter, and Deicke); hydrochloride, m.p.  $235-237^\circ$  (Cook and Hill).

The discrepancies may be due to the existence of stereoisomeric forms, which have not yet been characterised. Cook and Hill prepared the *phenylurethanes*, *benzoates*, *p-nitro*-, and *p-amino-benzoates* of their compounds, some of which had local anæsthetic activity.

Trimethylamine reacts with *ac-2-chloro-3-hydroxytetralin* to give *ac-3-hydroxy-2-tetrahydronaphthyltrimethylammonium chloride*, m.p. 243° (decomp.), resembling choline in properties; the corresponding base is strongly alkaline (Bamberger, Lodter, and Deicke; cf. von Braun and Weissbach, Ber. 1930, 63 [B], 3052).

**Dihydronaphthalene Glycols and Oxides.**—By hydrolysis of *ac-2-bromo-1-hydroxytetralin* with aqueous alkali, Strauss and Rohrbacher obtained what they consider to be the *trans*-form of *ac-1:2-dihydroxytetralin*, m.p. 112–113°; *diacetate*, m.p. 84°. The isomeric *cis*-form is obtained by careful oxidation of  $\Delta^1$ -dihydronaphthalene with potassium permanganate; it has m.p. 101.5–102° and its *diacetate* m.p. 78.6–79.2°. A mixture of the stereoisomeric acetates is obtained when *ac-1:2-dibromotetralin* is treated with glacial acetic acid and potassium acetate.

The glycol of  $\Delta^2$ -dihydronaphthalene, *ac-2:3-dihydroxytetralin*, is also known in at least two forms. One form, crystallising in silvery plates, m.p. 135°, is obtained by the action of potassium carbonate on the 2:3-dibromotetralin, by hydrolysis of the 2:3-oxide, and also from the 2:3-chlorohydrin. Leroux (l.c.) considered this to be the *cis*-form, but Strauss and Rohrbacher think it is the *trans*-form as it has the higher melting-point of the two. Its *diacetate* has m.p. 109.5–110°, *dibenzoate*, 89–90° (Bamberger and Lodter, l.c.). Leroux, by treating *ac-2:3-dibromotetralin* with silver acetate in acetic acid solution obtained an acetate giving on hydrolysis a mixture of glycols from which he separated (1) an isomeric *ac-2:3-dihydroxytetralin*, striated tablets m.p. 120°, giving a *diacetate*, m.p. 59°, *dibenzoate*, m.p. 126°, and (2) a substance, m.p. 140°, which he considered to be a compound of the two glycols. On oxidation, these glycols give *o-phenylenediacetic acid*.

*ac-1:3-Dihydroxytetralin* is one of the products of the action of alkalis on the 2:3-chlorohydrin; it has m.p. 49°, b.p. 175–178°/20 mm.

The oxides of  $\Delta^1$ - and  $\Delta^2$ -dihydronaphthalene are analogous in their methods of formation and properties to ethylene oxide.  $\Delta^1$ -*Dihydronaphthalene oxide* (1:2-*epoxytetralin*), is formed quantitatively by the action of cold alcoholic potash on *ac-2-bromo-1-hydroxytetralin*, into which it is reconverted by hydrogen bromide. It is a mobile liquid with a naphthalene-like odour, b.p. 86–88°/1–2 mm., m.p. 20–21°, and polymerises readily, for instance when distilled *in vacuo*, to a colourless resin, being much less stable than the 2:3-oxide. It isomerises when treated with dry hydrogen chloride in a solvent to  $\beta$ -tetralone, but not quantitatively. When hydrogenated it gives *ac-tetrahydro- $\beta$ -naphthol* (Strauss and Rohrbacher, l.c.).  $\Delta^2$ -*Dihydronaphthalene oxide* (2:3-*epoxytetralin*) is a dimorphous

crystalline substance, m.p. 43.5°, b.p. 257–259°/715 mm., volatile with steam (Bamberger and Lodter, l.c.; Cook and Hill, l.c.). It is one of several products of the action of alkalis on the 2:3-chlorohydrin, and apparently undergoes isomerisation to form 1:2-dihydro-2-naphthol, which is another product of the reaction. According to Cook and Hill, the best method of preparing the 2:3-oxide is by the action of perbenzoic acid on  $\Delta^2$ -dihydronaphthalene in chloroform; the yield is 85%.

#### DERIVATIVES OF MIXED AROMATIC-ALICYCLIC CHARACTER.

By the reduction to tetralin derivatives of heteronuclear di-substituted naphthalenes, compounds of mixed aromatic-alicyclic character are obtained. Thus Bamberger and Hoskyns-Abraham (Ber. 1889, 22, 943) reduced 1:5-naphthylenediamine with sodium and amyl alcohol, and obtained *tetrahydro-1:5-naphthylenediamine*, m.p. 77°, a strong base which darkens in air, and forms a crystalline carbonate, hydrochloride, and sulphate; the *diacetyl* derivative has m.p. 262°. With carbon disulphide in cold ether solution it forms a *thiocarbamate*, m.p. 145°, which when boiled with alcohol loses hydrogen sulphide to give *diamino-bis-tetrahydronaphthylthiocarbamide*, which sinters at 120°, m.p. 155°. One amino-group of the tetrahydro-1:5-diamine is diazotisable, and from it can be prepared 5-amino-5:6:7:8-tetrahydro-1-naphthol, an oil of sharp ammoniacal odour which absorbs carbon dioxide from the air; *hydrochloride*, m.p. 220°; *diacetyl* derivative, m.p. 151–151.5° (Bamberger and Bammann, *ibid.*, p. 951).

Reduction of 2:6- and 2:7-naphthylenediamines with sodium and amyl alcohol gives *tetrahydro-2:6-naphthylenediamine*, m.p. 61° (*diacetyl*, m.p. 240°) and *tetrahydro-2:7-naphthylenediamine*, m.p. ca. 60° (*diacetyl*, m.p. 203°). Similar reduction of 2-amino-7-naphthol and of 2-amino-7-methoxynaphthalene gives a mixture of the two possible tetrahydro derivatives. The following are described by Windaus *et al.* (*ibid.* 1924, 57 [B], 1731):

2-Amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene, m.p. 168–169°; *picrate*, m.p. 205°; *acetyl*, m.p. 195°; *dibenzoyl*, m.p. 174°; 6:8-dibromo derivative, m.p. 251° (decomp.); a mononitro-, m.p. 236° (decomp.), and 6:8-dinitro- derivative, m.p. 243° (decomp.).

2-Amino-7-hydroxy-5:6:7:8-tetrahydronaphthalene, m.p. 141–142°; *picrate*, m.p. 181°.

2-Amino-7-methoxy-1:2:3:4-tetrahydronaphthalene, liquid; *hydrochloride*, m.p. 213°; *picrate*, decomp. 212°.

2-Amino-7-methoxy-5:6:7:8-tetrahydronaphthalene, *picrate*, m.p. 183°; *acetyl*, m.p. 93°.

2-Hydroxy-7-methoxy-1:2:3:4-tetrahydronaphthalene, m.p. 71°, is prepared by hydrogenation of 2-hydroxy-7-methoxynaphthalene in the presence of spongy platinum.

Long and Burgor obtained 1-hydroxy-6-methoxy-1:2:3:4-tetrahydronaphthalene by hydrogenating 6-methoxy-1-tetralone; it has b.p. 109°/1 mm.; *a-naphthylurethane*, m.p. 131–133° (J. Org. Chem. 1941, 6, 852).

## ALKYL HOMOLOGUES OF TETRALIN.

A few workers have studied the hydrogenation of alkylnaphthalenes, by which dihydro- and tetrahydro-alkylnaphthalenes are produced, and, in addition, alkyltetralins have been obtained by the following methods:

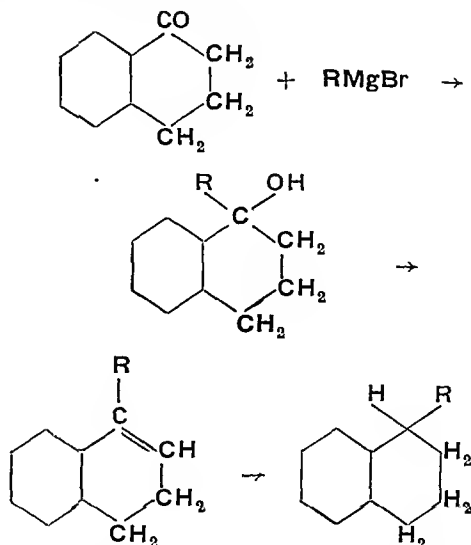
1. Condensation of alkyl halides with tetralin.
2. Reduction of the keto-group of acyltetralins.
3. From alkyl-substituted  $\alpha$ -tetralones by reduction or other operations.
4. Cyclisation of hydroxy derivatives (alcohols) of *n*-amylbenzene and their higher homologues.

From the comparatively small amount of work which has been reported on the reduction of alkylnaphthalenes, it appears that hydrogenation of the unsubstituted ring predominates. Thus, according to Veselý and Kapp, reduction of 1-methylnaphthalene gives a mixture containing 10% 5:8-dihydro-, the rest being a mixture of 5:6- and 7:8-dihydro-1-methylnaphthalenes; 2-methylnaphthalene gave 58% of 5:8-dihydro- and 42% of mixed 5:6- and 7:8-dihydro derivatives (Coll. Czech. Chem. Comm. 1931, 3, 448). Schroeter found that when  $\beta$ -methylnaphthalene is catalytically hydrogenated the product is 5:6:7:8-tetrahydro-2-methylnaphthaleno (Ber. 1921, 54 [B], 2242), an observation confirmed by Shreve and Lux (Ind. Eng. Chem. 1943, 35, 308), who used a Raney nickel catalyst in alcohol at 185°/1,200-1,740 lb. per sq. in., obtaining a mixture of *ar*-2-methyltetralin and 2-methyldecalin. Lévy obtained only 5:6:7:8-tetrahydro-2-ethylnaphthaleno by hydrogenation of 2-ethylnaphthalene in the presence of nickel prepared at 360° (Ann. Chim. 1938, [xi], 9, 5), but under other conditions the 1:2:3:4-tetrahydro-compound may be formed. The hydrogenation of 2:3-dimethylnaphthalene, using as catalyst active charcoal and ammonium molybdate with sulphur at 350°, was studied by Coulson (J.C.S. 1938, 1305); under these conditions the chief product was 5:6:7:8-tetrahydro-2:3-dimethylnaphthalene, but some 1:2:3:4-tetrahydro-compound was obtained (a mixture of *cis*- and *trans*-forms) and also some 2:3-dimethyldecalin.

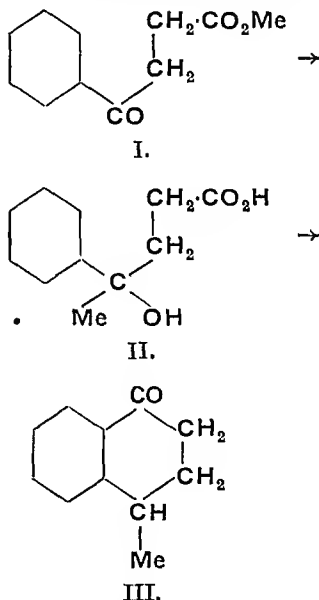
When tetralin is alkylated with alkyl chlorides or bromides in the presence of aluminium chloride or bromide, the entering alkyl group takes up a  $\beta$ -position, giving 2-alkyl-5:6:7:8-tetrahydronaphthalenes (Boedtker and Rambech, Bull. Soc. chim. 1924, [iv], 35, 631; Barbot, *ibid.* 1930, [iv], 47, 1314). Similarly with acyl chlorides,  $\beta$ -acyl derivatives of tetralin are formed, giving on reduction *ar*- $\beta$ -alkyltetralins (Barbot, *l.c.*). Tetralin can also be alkylated by means of olefins in the presence of aluminium chloride (I.G., B.P. 265601; 273665; 295990), and it can be condensed with butadiene (I.G., B.P. 315312).

Several authors have synthesised alkyltetralins by reduction of corresponding alkyl-1-tetralones which are obtained by cyclising suitably substituted  $\gamma$ -phenylbutyric acids (see tetralones). An additional alkyl group can be introduced by treating the tetralone with a Grignard reagent,

dehydrating to form a dihydronaphthalene and finally hydrogenating; thus



A modification of this process consists in treating methyl benzoylpropionate (I) with methyl magnesium iodide, to form a methyl carbinol (II) which is then dehydrated, reduced, and cyclised to a tetralone. Compound (III) is



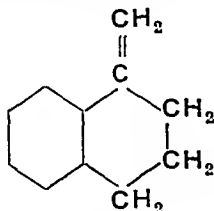
is again treated with a Grignard reagent and the resulting carbinol converted into a 1:4-dialkyltetralin (see Klotzel, J. Amer. Chem. Soc. 1940, 62, 1708). With suitable modifications the method is capable of giving a wide variety of alkylated tetralins.

The cyclisation of alcohols derived from *n*-amylbenzene by means of sulphuric and phosphoric acids has been studied by Roblin, Davidson, and Bogert, who showed that the same product, 1-methyl-1:2:3:4-tetrahydronaphthalene, was obtained whatever the position of the

hydroxyl group in the aliphatic chain (*ibid.* 1935, 57, 151). By the same process, using alcohols derived from higher alkylbenzenes, other *ac*-1-alkyltetralins were synthesised.

**Methyltetralins and their Derivatives.**  
—*ac*-1-Methyltetralin (1-methyl-1:2:3:4-tetrahydronaphthalene) is a liquid, b.p. 218–219° (Bogert, Roblin, and Davidson, *l.c.*).

An interesting hydrocarbon, 1-methylene-1:2:3:4-tetrahydronaphthalene,



was obtained by Schroeter by boiling *ac*-tetrahydronaphthylene-1-acetic acid,



with dilute sulphuric acid. It has b.p. 103°/14 mm.,  $d_4^{20}$  0.9836 (Ber. 1925, 58 [B], 713). It is also obtained, along with 1-methyl-3:4-dihydronaphthalene, by dehydrating *ac*-1-hydroxy-1-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 88–89° (von Auwers, *ibid.*, p. 151; Annalen, 1918, 415, 98). 1:2-Dihydroxy-1-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 75–76°, is obtained by oxidising *ac*-1-methyldihydronaphthalene.

*ar*-2-Methyltetralin has been prepared by the catalytic reduction of 2-methylnaphthalene (*supra*); it has b.p. 220–222° (Schroeter), 224–226° (Krollpfeiffer and Schäfer, who obtained it from 7-methyl-1-tetralone, Ber. 1923, 56 [B], 620).

*ar*-2-Methyltetralin when sulphonated gives the 3-sulphonic acid (amide, m.p. 155°, Shreve and Lux, J. Amer. Chem. Soc. 1943, 35, 308) and when acetylated in the presence of aluminium chloride the 3-acetyl derivative, b.p. 156–157°/11 mm. (Karrer and Epprecht, Helv. Chim. Acta, 1940, 23, 275). The sulphonic acid by caustic soda fusion gives *ar*-2-methyl-3-hydroxytetralin, m.p. 89°.

*ar*-Tetrahydro-1-naphthylmethylamine is obtained, together with much tetralin, by reduction

of *ar*-tetrahydro- $\alpha$ -naphthonitrile with sodium and alcohol; it has b.p. 149–162°/11 mm., *acetyl*, m.p. 125°, *benzoyl*, m.p. 144° (von Braun *et al.*, Ber. 1922, 55 [B], 1700). It is obtained (in 90% yield) by reduction of  $\alpha$ -naphthylmethylamine with sodium and amyl alcohol, and by catalytic hydrogenation of *ar*-tetrahydro- $\alpha$ -naphthonitrile in tetralin solution. The benzoyl derivative is converted by phosphorus pentachloride into *ar*-1-chloromethyltetralin, m.p. 50–51°, b.p. 144–145°/13 mm. (von Braun, Gruber, and Kirschbaum, *ibid.*, p. 3664).

*ar*-2-Amino-1-methyltetralin has been obtained by sodium-amyl alcohol reduction of 1-methyl-2-naphthylamine; it has b.p. 170–175°/30 mm.; *acetyl*, m.p. 134°, *benzoyl*, m.p. 222° (Mayer and Schnecko, *ibid.* 1923, 56 [B], 1408).

The isomeric *ac*-tetrahydro- $\alpha$ -naphthylmethylamine, b.p. 269–270°/722 mm. is formed when  $\alpha$ -naphthonitrile is reduced with sodium and alcohol; the *benzoyl* derivative has m.p. 125–126°; *picrate*, m.p. 170° (von Braun, Gruber, and Kirschbaum, *l.c.*; Bamberger and Lødter, *ibid.* 1887, 20, 1702; Bamberger and Helwig, *ibid.* 1889, 22, 1912). It is a strong base.

*ar*-Tetrahydro-2-naphthylmethylamine is obtained by similar methods to those described for the tetrahydro-1-naphthylmethylamine; it has b.p. 146–148°/11 mm., *benzoyl* derivative, m.p. 165°, *picrate*, m.p. 215° (von Braun *et al.*, *l.c.*). *ar*-1-Amino-2-methyltetralin, m.p. 158–161° (*acetyl*, m.p. 185–186°), was obtained by Veselý and Kapp by sodium-amyl alcohol reduction of 2-methyl- $\alpha$ -naphthylamine, and from it, in small yield, *ar*-1-hydroxy-2-methyltetralin was prepared (Coll. Czech. Chem. Comm. 1931, 3, 448).

*ac*-Tetrahydro-2-naphthylmethylamine is obtained, with by-products, when  $\beta$ -naphthonitrile is reduced with sodium and alcohol. It is a strongly basic liquid, b.p. 270.2°/729 mm.; *acetyl* derivative, m.p. 64–65°. Many derivatives were described by Bamberger *et al.* (Ber. 1887, 20, 1711; 1889, 22, 1912).

Some higher alkylated tetralins which have been described in the literature are listed in the following table, but it must be remarked that not a few such compounds, and also alkylidihydronaphthalenes, have been prepared in the

TABLE OF ALKYLATED TETRALINS.

(a) Alkyl Group in Hydrogenated Ring.

1:2:3:4-Tetrahydro-naphthalene.	B.p.	Method of preparation.	Reference.
1-Ethyl-	237–238°	Cyclisation of phenylalkyl alcohols.	Roblin, Davidson, and Bogert, J. Amer. Chem. Soc. 1935, 57, 151.
2-Ethyl-	235–235.5°/731 mm.	Reduction of tetralone.	Lévy, Ann. Chim. 1938, [xii], 9, 5.
1- <i>n</i> -Propyl-	258°	As for 1-ethyl.	Roblin, Davidson, and Bogert, <i>l.c.</i>
1- <i>iso</i> Propyl-	247°	"	"
1:2-Dimethyl-	235°	"	"
2:2-Dimethyl-	104°/12 mm.	Synthesis from benzene and dimethylsuccinic anhydride.	Clemo and " Dickenson, J.C.S. 1937, 255.
	123°/34 mm.	"	Sengupta, J. pr. Chem. 1938, [ii], 151, 82.
2:2-Diethyl-	110°/4 mm.	Synthesis.	Kloetzel, J. Amer. Chem. Soc. 1940, 62, 3405.
1:1:4-Trimethyl-	68°/0.2 mm.	"	"

(b) *Alkyl Group in Aromatic Ring.*

5:6:7:8-Tetrahydro-naphthalene.	M.p. or B.p.	Method of preparation.	Reference.
2-Ethyl-	B.p. 245–246° 239–239.5°/736 121–122°/10 mm.	Reduction of the tetralone.  Tetralin and EtBr.	Krollpfeffer and Schäfer, Ber. 1923, 56 [B], 620. Lévy, <i>l.c.</i> Barbot, Bull. Soc. chim. 1930, [iv], 47, 1314. Coulson, J.C.S. 1938, 1305.
2:3-Dimethyl-	M.p. 10° B.p. 244–246° B.p. 128°/7 mm.	Synthesis from <i>o</i> -xylene.	Barnett and Saunders, <i>ibid.</i> 1933, 434.
2-Methyl-3-ethyl-	B.p. 127–128°/11 mm.	Acetylation of 2-methyl-tetralin.	Karrer and Epprecht, Helv. Chim. Acta, 1940, 23, 275.
1:4-Dimethyl- 1:3-Dimethyl- 2-isoPropyl- "	B.p. 254°/760 mm. B.p. 250–252° B.p. 124–126°/13 mm. B.p. 255°/760 mm.	Synthesis from <i>p</i> -xylene. Reduction of the tetralone. Tetralin and alkyl halide. " "	Barnett and Saunders, <i>l.c.</i> " " Boedtke and Rambech, Bull. Soc. chim. 1924, [iv], 35, 631.
2-tert.-Butyl- "	B.p. 129°/11 mm. B.p. 265.5°/760 mm.	" "	Barbot, <i>l.c.</i> Boedtke and Rambech, <i>l.c.</i>
2-Docosyl- (CH <sub>3</sub> ·[CH <sub>2</sub> ] <sub>21</sub> ).	M.p. 43–45°	Tetralin and behenyl chloride.	Mikeska and Cohen, J. Org. Chem. 1941, 6, 792.

(c) *Alkyl Groups in both Aromatic and Hydrogenated Rings.*

1:2:3:4-Tetrahydro-naphthalene.	M.p. or B.p.	Method of preparation.	Reference.
2:6-Dimethyl-	M.p. 14–17° B.p. 237–239°	Hydrogenation of dimethyl-naphthalene.	Coulson, J.C.S. 1935, 77.
2:7-Dimethyl- 2:5-Dimethyl-	B.p. 237–238° B.p. 110–111°/11 mm.	" "	Mayer and Schulte, Ber. 1922, 55 [B], 2164.
1:6-Dimethyl- 2:2:7-Trimethyl- 1:1:2:6-Tetramethyl- (Irene)	B.p. 128°/23 mm. B.p. 120–125°/10 mm.	Synthesis. "	Sengupta, <i>l.c.</i> Bogert and Apfelbaum, J. Amer. Chem. Soc. 1938, 60, 930.

course of researches directed towards other ends, such as the synthesis of alkylated naphthalenes, and of natural products such as sesquiterpenes and resins.

The hydrogenated alkyltetralins are converted by heating with sulphur or selenium at a high temperature (200–300°) into alkynaphthalenes. When two alkyl groups are attached to one carbon atom in the tetralin, one of these is lost during dehydrogenation, although it is to be noted that Sengupta found it necessary to heat 2:2-dimethyl-1:2:3:4-tetrahydronaphthalene in a sealed tube at 300–320° to obtain 2-methyl-naphthalene from it. Kloetzel described 1:1:4-trimethyltetralin as having a pungent camphoraceous odour; by dehydrogenation he obtained 1:4-dimethylnaphthalene.

Darzens and Levy synthesised 4-methyl-1:2:3:4-tetrahydronaphthalene-1-carboxylic acid, m.p. 87°, and found that when dehydrogenated by sulphur or selenium it lost the carboxyl group giving 1-methylnaphthalene (Compt. rend. 1934, 199, 1133).

Coulson (*l.c.*) studied the sulphonation of *ar*-2:3-dimethyl- and 2:6- and 2:7-dimethyl-tetralins and obtained the following compounds:

- ar*-2:3-Dimethyltetralin-1-sulphonic acid;  
amide, m.p. 135°.
- ar*-2:6-Dimethyltetralin-7-sulphonamide,  
m.p. 166–167°.
- ar*-2:7-Dimethyltetralin-6-sulphonamide,  
m.p. 145.5°.

The following compounds were also prepared:

- ar*-3:7-Dimethyltetrahydro- $\beta$ -naphthol,  
m.p. 116°.
- ar*-3:6-Dimethyltetrahydro- $\beta$ -naphthol,  
m.p. 87°.
- ar*-2:6-Dimethyltetralin-7-carboxylic acid,  
m.p. 183°.
- ar*-2:7-Dimethyltetralin-6-carboxylic acid,  
m.p. 187°.

6- and 7-Methoxy-2-ethyl-1:2:3:4-tetrahydronaphthalene were prepared by Lévy by a synthetic method (Ann. Chim. 1938, [xi], 9, 5).

The benzo- $\Delta^{10(11)}$ -nor-*p*-menthene of Kay and Morton (J.C.S. 1914, 105, 1565) is ac-1-isopropenyltetralin, a liquid with a pronounced odour of cedrene, b.p. 259–261°/745 mm.

## TETRALIN ALDEHYDES.

The two *ar*-tetralin aldehydes have been prepared by oxidising *ar*-1- and -2-methyltetralins with chromyl chloride in carbon disulphide solution (Fleischer and Feldmeier, Ber. 1922, 55 [B], 3290), and by oxidising the corresponding *ar*-tetrylcarbinols with dichromate in sulphuric acid (von Braun *et al.*, *ibid.*, p. 1700); and the  $\beta$ -aldehyde by oxidising the chloromethyl compound (I.G., B.P. 353260).

*ar*-Tetrahydro- $\alpha$ -naphthaldehyde is an odourless liquid, b.p. 131–133°/12 mm.; *semi-carbazone*, m.p. 187° (von Braun).

*ar*-Tetrahydro- $\beta$ -naphthaldehyde has an



odour of peppermint, b.p. 138°/14 mm. (von Braun); 142–143°/11 mm.; *semicarbazone*, m.p. 222–223° (I.G., B.P. 353260).

The Reimer-Tiemann reaction on *ar*- $\beta$ -tetralol (Woodward, J. Amer. Chem. Soc. 1940, 62, 1208) and also the action of anhydrous hydrogen cyanide and hydrogen chloride in presence of zinc chloride (Thoms and Kross, Arch. Pharm. 1927, 265, 330) give an aldehyde, shown by Arnold, Zangg, and Sprung (J. Amer. Chem. Soc. 1941, 63, 1314) to be *ar*-2-*hydroxytetrahydro-1-naphthaldehyde*, m.p. 86–87° (the earlier authors gave 80–82°), *oxime*, m.p. 150°, *phenylhydrazone*, m.p. 180°. *ar*-2-*Hydroxytetrahydro-3-naphthaldehyde*, made by Arnold *et al.*, by catalytic reduction of 2-acetoxy-3-naphthoyl chloride, has m.p. 56–57°; *oxime*, m.p. 105–106–5°.

#### TETRAHYDRONAPHTHOIC ACIDS.

When  $\alpha$ - and  $\beta$ -naphthoic acids or their sodium salts are reduced with sodium and alcohol they undergo hydrogenation in the ring carrying the carboxyl group, forming successively *ac*-dihydro- and -tetrahydro-naphthoic acids. A labile dihydro-acid is first formed, and this can be changed to a stable form by heat or, more quickly, by boiling in alkaline solution (*cf.* 1:4- and 1:2-dihydronaphthalenes). When catalytic hydrogenation is applied to the naphthoic acids, however, using a nickel catalyst, according to Ipatiew the  $\alpha$ -acid loses its carboxyl group and forms tetralin, whilst the  $\beta$ -acid gives mainly *ar*-tetrahydro- $\beta$ -naphthoic acid which by further treatment gives decalin and decahydro- $\beta$ -naphthoic acid (Ber. 1909, 42, 2100). When ethyl  $\alpha$ -naphthoate is reduced with sodium and alcohol the carboxyl group is attacked and methyl-dihydronaphthalene formed (de Pomereau, Compt. rend. 1921, 172, 1503). Reduction of the  $\alpha$ -carboxyl group was also observed by Willstätter and Jaquet when hydrogenating naphthalic anhydride in presence of platinum, two of the products being tetrahydro-1-methylnaphthalene-8-carboxylic acid, m.p. 150°, and decahydroacenaphthene (Ber. 1918, 51, 767, 774).

Both  $\alpha$ - and  $\beta$ -naphthonitriles when hydrogenated in presence of nickel compounds give only naphthylmethyamines, the nucleus not being attacked (von Braun, Blessing, and Zobel, *ibid.* 1923, 56 [B], 1988).

*ar*-Tetrahydro- $\alpha$ -naphthoic Acid, m.p. 150°, was obtained by hydrolysing with fuming hydrochloric acid *ar*-tetrahydro- $\alpha$ -naphthonitrile, m.p. 48°, which was prepared from *ar*-tetrahydro- $\alpha$ -naphthylamine (von Braun, *ibid.* 1922, 55 [B], 1700). The product prepared similarly by Bamberger and Bordt (*ibid.* 1889, 22, 625) was presumably impure.

*ar*-Tetrahydro- $\beta$ -naphthoic Acid, m.p. 151°, was obtained by von Braun by oxidation of the  $\beta$ -aldehyde with potassium permanganate (*l.c.*) and also (m.p. 152–153°) as sole product of the reaction between tetralin and oxalyl chloride in the presence of aluminium chloride (von Braun, Kirschbaum, and Schuhmann, *ibid.* 1920, 53 [B], 1155). Newman and Zahm (J. Amer. Chem. Soc. 1943, 65, 1097) give the m.p. 154–155°; *methyl ester*, b.p. 149–150°/4 mm.

It is further hydrogenated by sodium and amyl alcohol to *decahydro- $\beta$ -naphthoic acid*, m.p. 79°. *ar*-Tetrahydro- $\beta$ -naphthoyl chloride is an oil, b.p. 162°/13 mm.; *amide*, m.p. 137–138°. *ar*-Tetrahydro- $\beta$ -naphthonitrile has m.p. 20–21°, b.p. 151–152°/11 mm.

*ac*-Tetrahydro- $\alpha$ -naphthoic Acid.—The reduction of  $\alpha$ - and  $\beta$ -naphthoic acids by sodium amalgam and sodium and alcohol was studied by von Sowinski (Ber. 1891, 24, 2354) and by Baeyer (Annalen, 1891, 266, 169) who showed that the former's products were not completely purified. Reduction of sodium  $\alpha$ -naphthoate in aqueous solution with sodium amalgam in a current of carbon dioxide gives as main product a labile dihydro- $\beta$ -naphthoic acid, probably 1:4-dihydro-2-naphthoic acid, m.p. 91°, which forms a *dibromide* (*ac*-dibromotetrahydro- $\beta$ -naphthoic acid), m.p. 132°. The labile acid when boiled with sodium hydroxide is converted into a stable acid, 3:4-dihydro-1-naphthoic acid (constitution confirmed by Kay and Morton, J.C.S. 1914, 105, 1565), m.p. 125°, giving *ac*-1:2-dibromotetrahydro-2-naphthoic acid, m.p. 152°.

*ac*-Tetrahydro- $\alpha$ -naphthoic acid is formed by further reduction of the dihydro acids or of  $\alpha$ -naphthoic acid with sodium and amyl alcohol, or best by reducing  $\alpha$ -naphthoic acid in absolute alcohol with five times the theoretical amount of sodium, the crude product being purified by careful oxidation with cold permanganate in sodium carbonate solution to remove dihydro acid (Kay and Morton, *l.c.*). It has m.p. 85°; *amide*, m.p. 116°, *ethyl ester*, b.p. 279°/747 mm. When brominated, the ethyl ester forms *ethyl ac*-1-bromotetralin-1-naphthoate, b.p. 208°/20 mm. (decomp.), which is converted by boiling diethylaniline (removal of hydrogen bromide) to *ethyl 3:4-dihydro-1-naphthoate*, b.p. 300–310°/756 mm. Kay and Morton used this compound for synthesising compounds of the benzoterpene series.

*ac*-Tetrahydro- $\beta$ -naphthoic Acid, formed by reduction of  $\beta$ -naphthoic acid with sodium and amyl alcohol, has m.p. 96° (Baeyer, *l.c.*).

*Menthyl esters* of *ac*- $\alpha$ - and *ac*- $\beta$ -tetrahydro-naphthoic acids are described by Rupe and Munter (Annalen, 1910, 373, 122).

1-Amino-5:6:7:8-tetrahydro-8-naphthoic Acid, m.p. 150–161° (decomp.), is obtained by reduction of naphthastyril with sodium amalgam in alkaline solution. It does not form a lactam, but with acetic acid gives *acetyl*tetrahydronaphthastyril, m.p. 103–104°, as well as 1-acetamido-5:6:7:8-tetrahydro-8-naphthoic acid, m.p. 181–182° (Schroeter and Rössler, Ber. 1902, 35, 4222).

#### TETRAHYDRONAPHTHALENEDICARBOXYLIC ACIDS.

*ac*-Tetrahydronaphthalene-2:3-dicarboxylic Acid was obtained by Baeyer and Perkin by a synthetic method (*ibid.* 1884, 17, 448; J.C.S. 1888, 53, 11, 20) and by R. D. Haworth and Slinger by reduction of naphthalene-2:3-dicarboxylic acid (*ibid.* 1940, 1321). The latter authors converted their product into anhydride by the action of acetyl chloride and separated this into *cis*- and *trans*-forms, from which they prepared acids and esters. From their work it appeared that the synthetic product of Baeyer



and Perkin was the *cis*-form. *cis*-ac-Tetrahydro-naphthalene-2:3-dicarboxylic acid has m.p. 194–195°, *anhydride*, m.p. 183°, *methyl ester*, m.p. 68–68.5°; the *trans*-acid has m.p. 226–227°, *anhydride*, m.p. 225–226°, *methyl ester*, m.p. 44.5–45.0°. The *cis*-acid was separated into *d*- and *l*-forms through their strychnine salts; the rotations of the acids in chloroform are  $[\alpha]_D^{16} + 85.5^\circ$  and  $-85^\circ$  respectively.

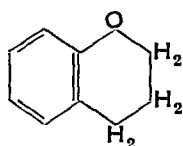
Tetrahydronaphthalene-1:8-dicarboxylic Acid is obtained by hydrogenating naphthalic acid, its salts, *anhydride* or *ester* but, as stated above, other products are formed according to the conditions (see p. 429a). Casares and Renedo (Anal. Fis. Quim. 1922, 20, 519) state that methyl and ethyl naphthalates are more readily reduced than the parent acid. Zengalis (Ber. 1894, 27, 2694) used red phosphorus and hydriodic acid to reduce naphthalic acid to the tetrahydro-acid. Sodium naphthalate can be hydrogenated to the tetrahydro derivative in the presence of a nickel catalyst at 200° (Schering-Kahlbaum A.-G., B.P. 353373). Tetrahydronaphthalene-1:8-dicarboxylic acid has m.p. 196°; *anhydride*, m.p. 119.5° (does not form an imide); *methyl ester*, m.p. 74°; *ethyl ester*, m.p. 52°; *ethyl hydrogen ester*, m.p. 48°.

Tetrahydronaphthalene-1:5-dicarboxylic Acid has m.p. 237.5–238.5°; the *methyl* and *ethyl esters* are liquids (Moro, Gazzetta, 1896, 26, i, 89).

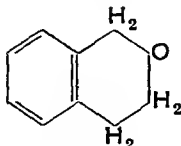
ac-Tetrahydronaphthalene-1:2-dicarboxylic Acid has m.p. 173° (slow heating), 193° (rapid heating); *anhydride*, m.p. 66–67° (Auwers and Möller, J. pr. Chem. 1925, [ii], 109, 124).

#### TETRALONES.

Corresponding with  $\alpha$ - and  $\beta$ -tetralols, which are secondary alcohols, are the ketones,  $\alpha$ - and  $\beta$ -tetralones or  $\alpha$ - and  $\beta$ -ketotetralins. These



$\alpha$ -tetralone.



$\beta$ -tetralone.

compounds have at present no technical importance, but  $\alpha$ -tetralone and its substitution products are of considerable interest as synthetic intermediates, for example in researches on the synthesis of substances related to sterols and sex hormones.  $\beta$ -Tetralone is much less stable than the  $\alpha$ -ketone.

$\alpha$ -Tetralone.—This compound has been obtained by several different processes. It was first prepared synthetically by the action of aluminium chloride on  $\gamma$ -phenylbutyryl chloride by Kipping and Hill (J.C.S. 1899, 75, 144) and later it was shown by Krollpfeiffer and Schäfer (Ber. 1923, 56 [B], 620) that  $\gamma$ -phenylbutyric acid can be cyclised to  $\alpha$ -tetralone in concentrated sulphuric acid at 100°. Schroeter obtained  $\alpha$ -tetralone by oxidising tetralin with chromic acid in dilute acetic acid (G.P. 346948) and it is formed in small amount,

together with *ar*-tetrahydro- $\alpha$ -naphthol and tetralin, in the catalytic hydrogenation of  $\alpha$ -naphthol (Schroeter, Annalen, 1922, 426, 88; G.P. 352720). It can also be obtained by oxidising the bromohydrin of 1:2-dihydronaphthalene with sodium dichromate and sulphuric acid to 2-bromo-1-tetralone, m.p. 40°, b.p. 144°/0.5–1.0 mm. (see Straus *et al.*, Annalen, 1925, 444, 165); (*oxime*, m.p. 136.5–137°), and reducing this with zinc dust and alcohol (Straus and Rohrbacher, Ber. 1921, 54 [B], 40).

$\alpha$ -Tetralone is a steam-volatile, colourless, mobile oil with an odour resembling camphor when cold and peppermint when warm, b.p. 131–133°/13 mm., 257°/760 mm.,  $\rho_{17}^{17}$  1.095,  $n_D^{17}$  1.570. It forms a *semicarbazone*, m.p. 217–220°, *phenylhydrazone* (unstable), m.p. 84–85°, *p*-bromophenylhydrazone, m.p. 117–118°; *oxime*, m.p. 103°. According to Inoue, the *oxime* of the ketone obtained by catalytic reduction of  $\alpha$ -naphthol is separable into two isomers, m.p. 88–89° and 102–103°, respectively (J. Chem. Ind. Japan, 1923, 26, 1335).

*Reactions and Derivatives.*— $\alpha$ -Tetralone shows the general reactivity of a ketone. It can be reduced to  $\alpha$ -tetralol with sodium and alcohol, and to tetralin by the Clemmensen method. By heating with sulphur (Darzens and Lévy, Compt. rend. 1932, 194, 181) or selenium (Ruzicka, Helv. Chim. Acta, 1936, 19, 421) it is dehydrogenated to  $\alpha$ -naphthol. The methylene group adjacent to the keto-group is active, and consequently  $\alpha$ -tetralone reacts with aldehydes. It forms a *monobenzylidene* derivative, m.p. 206–207° (Wallach and Weissenbach, Annalen, 1924, 437, 148), 2-cinnamylidene-1-tetralone, yellow, m.p. 132–134°, and a *bis-terephthaldehyde* derivative, m.p. (indefinite) 240–255° (Herzog and Kreidl, Ber. 1922, 55 [B], 3394); and condenses similarly with *p*-dialkylaminobenzaldehydes (Shriner and Teeters, J. Amer. Chem. Soc. 1938, 60, 936). With isatin- $\alpha$ -anil it condenses to give a blue dye of indigoid type, and behaves similarly with thionaphthenequinone- $\alpha$ -anil (Herzog and Kreidl, *l.c.*), but with isatin itself the reaction goes beyond the initial condensation stage and 5:6-dihydro- $\alpha$ -naphthacridine-7-carboxylic acid is formed (von Braun and Wolff, Ber. 1922, 55 [B], 3675).

The reaction between  $\alpha$ -tetralone and ethyl oxalate furnishes *ethyl  $\alpha$ -tetralone-2-glyoxalate*, m.p. 98°, whence *ethyl  $\alpha$ -tetralone-2-carboxylate* (or 1-hydroxy-3:4-dihydronaphthalene-2-carboxylate), m.p. 34°, is obtained (W. Hüchel and E. Goth, *ibid.* 1924, 57 [B], 1285). The further condensation of this last compound with esters of  $\alpha$ -halogenated fatty acids, *e.g.*, to give  *$\alpha$ -tetralone-2-acetic acid*, m.p. 109–110°, has been studied by Bergs (*ibid.* 1930, 63 [B], 1285).  $\alpha$ -Tetralone reacts with ethyl formate in the presence of sodium to give 2-hydroxymethyl-1-tetralone, b.p. 153.5–153°/10 mm. (von Auwers and Weigand, J. pr. chem. 1932, [ii], 134, 82) and also reacts with formaldehyde and dialkylamines to give 2-dialkylaminomethyl derivatives (Mannich *et al.*, Arch. Pharm. 1937, 275, 54). For the reaction between 2-bromo-1-tetralone and sodiomalonic esters, see Schroeter and Gluschke, B.P. 323187. Dane and her col-

laborators have studied the reaction between 6-methoxy-1-tetralone and acetylaryl magnesium bromide to give 6-methoxy-1-vinyl-3:4-dihydronaphthalene (Annalen, 1937, 532, 39).

By chlorination of  $\alpha$ -tetralone a mono-, m.p. 45°, and a di-chloro- $\alpha$ -tetralone, m.p. 75–76°, have been obtained (Tetralin G.m.b.H. and Riebensahm., G.P. 377587). Schroeter obtained 6-chloro-, m.p. 30–31°, and 7-chloro-1-tetralone by oxidising chlorinated tetralin. Nitration gives a mixture of 5-, m.p. 102.5°, and 7-nitro-1-tetralone, m.p. 106°, in the ratio 93:7 (Schroeter *et al.*, Ber. 1930, 63 [B], 1308).

The oximes of 1-tetralone and of the above chloro- and nitro-tetralones undergo a peculiar change when warmed with acetic acid and acetic anhydride in the presence of hydrogen chloride, being transformed into  $\alpha$ -naphthylamine or the corresponding chloro- or nitro- $\alpha$ -naphthylamine. When, however, there is an 8-substituent in the tetralone oxime, a kind of Beckmann change occurs and a lactam of  $\alpha$ -amino-phenylbutyric acid is formed (Schroeter, *l.c.*).

2-Hydroxy-1-tetralone, m.p. 36–36.5 (acetate, m.p. 74.5–75°), obtained from 2-bromo-1-tetralone, is very unstable in alkaline solution, undergoing autoxidation in presence of oxygen to form successively  $\beta$ -naphthoquinol, 3:4:3':4'-tetrahydroxy-1:1'-dinaphthyl and 2-hydroxy-[ $\alpha$ ]-naphthoquinone (Strauss, Bernoulli, and Mautner, Annalen, 1925, 444, 165; cf. Weissberger and Schwarze, *ibid.* 1931, 487, 53). 5-Hydroxy-, 8-hydroxy-, and 5-acetamido-1-tetralone have been obtained by catalytic reduction of 1:5-dihydroxy-, 1:8-dihydroxy-, and 1:5-acetamidohydroxy-naphthalene respectively (Schroeter and Tetralin G.m.b.H., G.P. 352720, 1920). For other  $\alpha$ -tetralone derivatives, cf. von Braun (Annalen, 1926, 451, 49).

A number of homologues of  $\alpha$ -tetralone have been prepared, of which the following may be quoted:

2-Methyl-1-tetralone, b.p. 98°/3 mm.; semicarbazone, m.p. 199°; obtained by methylating  $\alpha$ -tetralone with sodamide and methyl iodide (English and Caviglieri, J. Amer. Chem. Soc. 1943, 65, 1089).

3-Methyl-1-tetralone, b.p. 94–96°/0.3 mm. (Bachmann and Struve, *ibid.* 1940, 62, 1618).

4-Methyl-1-tetralone, b.p. 110–111°/1 mm.; semicarbazone, m.p. 209–211°.

2:4-Dimethyl-1-tetralone, b.p. 112°/1 mm., odour of liquorice; semicarbazone, m.p. 218–220° (decomp.);

3:4-Dimethyl-1-tetralone, b.p. 96–97°/0.3 mm. (Kloetzel, *ibid.* 1940, 62, 1708).

2:3-Dimethyl-1-tetralone, m.p. –1°; b.p. 148–150°/17 mm. (Schroeter *et al.*, Ber. 1918, 51, 1602).

7-Methyl-1-tetralone, m.p. 32.5–33.5°; semicarbazone, m.p. 224–225°;

7-Ethyl-1-tetralone, b.p. 152–153°/12 mm.; semicarbazone, m.p. 223–225°;

5:7-Dimethyl-1-tetralone, m.p. 49–50°; semicarbazone, m.p. 234–235° (Krollpfeiffer and Schäfer, *ibid.* 1923, 56 [B], 620).

5:8-Dimethyl-1-tetralone, m.p. 23°; oxime, m.p. 143–144° (Schroeter *et al.*, *ibid.* 1930, 63 [B], 1308).

$\beta$ -Tetralone.—This compound has been obtained by the following methods: (1) by heating 1:4-dihydronaphthalene bromohydrin with magnesium carbonate or quinoline (Bamberger and Lotter, Annalen, 1895, 288, 112) probably via the 2:3-oxido; (2) by the action of dry hydrogen chloride on 3:4-dihydronaphthalone-1:2-oxido in light petroleum, by isomeric change (Straus and Rohrbacher, Ber. 1921, 54, [B], 40); (3) by heating  $\alpha$ -2-dimethylamino-1-tetralol methiodide slightly above its melting-point (von Braun, Braunsdorf, and Kirschlbaum, *ibid.* 1922, 55 [B], 3648); (4) by distilling the calcium salt of  $\alpha$ -phenyleneacetic-propionic acid (Einhorn and Lumsden Annalen, 1895, 286, 275); (5) by hydrolysis of 3:4-dihydro-2-naphthylurethane, obtained by the Curtius reaction from 3:4-dihydro-2-naphthoic acid (P. G. Crowley and R. Robinson, J.C.S. 1938, 2001); (6) by reducing 2-methoxynaphthalene to the 3:4-dihydro-compound with sodium and ethyl alcohol, followed by hydrolysis with dilute hydrochloric acid (Cornforth, Cornforth, and R. Robinson, *ibid.* 1942, 689).

Of these methods the last is probably the most convenient laboratory method. The yield of  $\beta$ -tetralone was 56% and the method is applicable to the production of substituted  $\beta$ -tetralones.

$\beta$ -Tetralone is a colourless, steam-volatile compound of agreeable odour, m.p. 18°, b.p. 138°/16 mm. (Bamberger and Lotter, *l.c.*), partially decomposed if distilled at ordinary pressure to naphthalene and water. It forms a bisulphite compound (unlike  $\alpha$ -tetralone), oxime, m.p. 87.5–88°, phenylhydrazone, m.p. 107.5–108° (decomp. by light), semicarbazone, m.p. 190–191°. In alkaline solution it undergoes rapid autoxidation, an indigo-blue colour developing.

$\beta$ -Tetralone forms a dibenzylidene derivative, m.p. 119–120° (Wallach and Weissenborn, Annalen, 1924, 437, 148). It can be methylated by means of methyl iodide and sodium isopropoxide in isopropyl alcohol to 1-methyl-2-tetralone (Cornforth, Cornforth, and Robinson, *l.c.*). With diazomethane it gives, however, 2-methylenetetrahydronaphthalene oxido (Mosetig and Burger, J. Amer. Chem. Soc. 1931, 53, 2295).

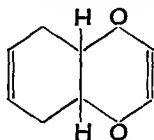
The following derivatives of 2-tetralone were described by Cornforth, Cornforth, and Robinson (*l.c.*): 1-methyl-, b.p. 137–138°/18 mm., semicarbazone, m.p. 200–202° (decomp.); 5-methoxy-, b.p. 120–122°/0.4 mm.; 6-methoxy-, m.p. 36.5°; 5-methoxy-1-methyl-, semicarbazone, m.p. 188–190°; 5-methoxy-1:1-dimethyl-, m.p. 83–85°, semicarbazone, m.p. 192–194°.

Highly chlorinated and brominated  $\beta$ -tetralones have been obtained by halogenation of 2-hydroxy-3-naphthoic acid; 1:1:3:3:4-pentachloro- $\beta$ -tetralone has m.p. 116°; 1:1:3:3-tetrachloro-4-acetoxy- $\beta$ -tetralone, m.p. 140° (Fries and Schimmolschmidt, Annalen, 1930, 484, 245).

$\alpha$ -Tetrahydro-[ $\alpha$ ]-naphthoquinone, yellow needles, m.p. 55.5°, is a substance closely resembling benzoquinone, and is prepared in a similar manner. It was obtained by Bamberger and Lengfeld (Ber. 1890, 23, 1131) by oxidising  $\alpha$ -tetrahydro- $\alpha$ -naphthylamine with chromic-sulphuric acid; it is also formed by similar

oxidation of *ar*-tetrahydro-4-hydroxy-1-naphthylamine (Jacobson and Turnbull, *ibid.* 1898, 31, 898) or of *ar*-tetrahydro-1:4-naphthylenediamine (Rowe and Green, J.C.S. 1918, 113, 961). The *bis*-chloroimide,  $C_{10}H_{10}(:NCl)_2$ , m.p. 68°, is obtained by the action of bleaching powder on *ar*-tetrahydro-1:4-naphthylenediamine in hydrochloric acid solution (Bamberger, Annalen, 1890, 257, 8). The quinone has also been obtained by electrolytic oxidation of *ar*-tetrahydro- $\alpha$ -naphthylamine (Ono, Mem. Coll. Sci. Kyoto, 1922, 5, 345). The *mono*-oxime of tetrahydro- $[\alpha]$ -naphthaquinone, m.p. 163°, is formed from tetrahydro- $\alpha$ -naphthol and nitrous acid; and the *monophenylhydrazine* is identical with 4-benzeneazo-*ar*-tetrahydro-1-naphthol (Rowe and Levin, J.C.S. 1927, 530). The quinone is reduced by sulphurous acid to the corresponding quinol, which can be re-oxidised by potassium dichromate successively to the quinhidrone and the quinone.

An isomeric tetrahydronaphthaquinone, namely, 5:8:9:10 *tetrahydro*- $[\alpha]$ -*naphthaquinone*,



m.p. 58°, is obtained by reaction of benzoquinone with butadiene (Diels, Alder, and Stein, Ber. 1929, 62 [B], 2337).

#### ACYL DERIVATIVES OF TETRALIN.

It has already been stated that tetralin reacts with acyl chlorides under Friedel-Crafts conditions in the  $\beta$ -position of the aromatic ring. According to Hesse, tetralin reacts slowly with acetyl chloride in carbon disulphide in the presence of aluminium chloride, giving a 90% yield, pure after one distillation, of *ar*- $\beta$ -*tetrahydronaphthyl methyl ketone*, a liquid, b.p. 182°/20 mm., forming a *semicarbazone*, m.p. 234–235° (*ibid.* 1920, 53 [B], 1645). Barbot (Bull. Soc. chim. 1930, [iv], 47, 1314) gives m.p. 257–258° for the *semicarbazone*; he also prepared *ar*- $\beta$ -*tetrahydronaphthyl ethyl ketone*, b.p. 169°/17 mm. (*semicarbazone*, m.p. 224–225°), the *n*-*propyl ketone*, b.p. 178°/18 mm., and the *isopropyl ketone*, b.p. 163°/11 mm. The ketones can be dehydrogenated by heating with sulphur to  $\beta$ -naphthyl alkyl ketones; according to von Braun, Hahn, and Seeman (Ber. 1922, 55 [B], 1687) they are dehydrogenated by heat alone at 680–700°. These authors used  $\beta$ -tetryl methyl ketone for the preparation of 2- $\beta$ -tetrahydronaphthylquinoline by condensation with isatin (*cf.* E. Schering, Emde, and Freund, G.P. 344027, 1920).  $\beta$ -Tetryl methyl ketone undergoes the Mannich reaction with formaldehyde and dimethylamine hydrochloride (Mannich and Lammering Ber. 1922, 55 [B], 3510). Tetralin also condenses with chloroacetyl chloride.

Although tetralin undergoes decomposition when warmed with a small proportion (1–2%) of aluminium chloride at 50–70° (Schroeter *et al.*, Ber. 1924, 57 [B], 190), it can be condensed with phthalic anhydride in the presence of

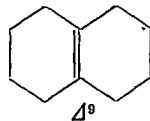
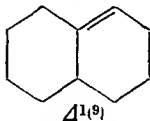
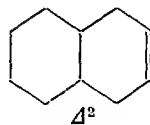
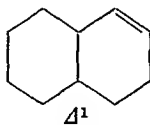
aluminium chloride in benzene at about 70° to give a quantitative yield of *o*-2-*tetraloylbenzoic acid*, m.p. 153–155°. Under similar conditions 2-methylnaphthalene forms *o*-2-*methyl-3-tetraloylbenzoic acid*, m.p. 160° (Schroeter, *ibid.* 1921, 54 [B], 2242). For the formation of indandiones from tetralin and dialkylmalonyl chloride, *see* von Braun *et al.*, *ibid.* 1920, 53 [B], 1161; Fleischer and Siefert, *ibid.*, p. 1255).

#### HEXAHYDRONAPHTHALENES.

Very little is definitely known about the hexahydronaphthalenes and it seems doubtful if one has yet been accurately characterised. The so-called hexahydronaphthalenes obtained by early workers by reduction of naphthalene with hydriodic acid were certainly mixtures. Preparations of hexalins have been made by removing halogen hydrides from dibromo- or dichloro-decalins, and by dehydrating octalin glycols. Leroux (Ann. Chim. 1910, [viii], 21, 473) obtained a product which he considered to be hexahydronaphthalene by heating dibromodecalin with quinoline but Morton and De Gouveia (J.C.S. 1934, 922) showed spectroscopically that the product so obtained contains 50% of tetralin and decalin. Borsche and Lange obtained hexahydronaphthalene, b.p. 75–85°/15 mm., by heating dichlorodecalin, b.p. 148–150°/15 mm., with aniline (Annalen, 1924, 434, 219). Nametkin and Glagoleff (Ber. 1929, 62 [B], 1570) dehydrated  $\Delta^{9:10}$ -octalin glycol by heating with dilute sulphuric acid at 150° and obtained hexahydronaphthalene as a liquid, b.p. 75–76°/8 mm.

#### OCTAHYDRONAPHTHALENES (OCTALINS).

According to current theory, six different octalins,  $C_{10}H_{16}$ , should exist, namely  $\Delta^1$ - and  $\Delta^2$ - (both in *cis*- and *trans*-forms),  $\Delta^{1(9)}$ - and  $\Delta^9$ -, thus:



In practice the octalins are generally prepared by dehydration of the  $\alpha$ - or  $\beta$ -decalols or their salts or esters and the product obtained is a mixture of isomers separable with some degree of difficulty. The  $\Delta^9$  appears to be the most stable isomer and others tend to change into it under the conditions of their formation; the  $\Delta^9$  isomer is in fact formed in the course of the dehydration of  $\beta$ -decalols, obviously through transformation of  $\Delta^1$  or  $\Delta^2$  isomers. It has also been shown that  $\Delta^{1(9)}$  changes into  $\Delta^9$  by heating with toluene-*p*-sulphonic acid in methyl alcohol (Hückel and Naab, Annalen, 1933, 502, 136), and that *trans*- $\Delta^2$ -octalin changes into  $\Delta^9$  when heated with phosphorus pentoxide (instead

*et al.*, J.C.S. 1937, 1136). The identity of the different octalins has been established mainly on the evidence given by their oxidation products. The octalins are generally characterised by their dibromides or nitrosochlorides. It must be noted, however, that an octalin can form two or possibly three different stereo-isomeric decalin derivatives by addition, which may account for a certain amount of confusion in the literature.

$\Delta^9$ -Octalin.—This octalin was obtained mixed with other isomers by Hückel, Danneel, Schwarz, and Gercke (Annalen, 1929, 474, 121) by dehydrating *cis*- $\beta$ -decalol with zinc chloride, and was prepared in quantity by similarly dehydrating mixed  $\beta$ -decalols at 180–195°. The mixed octalins so obtained were converted into nitrosochlorides, from which the blue crystalline nitrosochloride of the  $\Delta^9$ -octalin was separated and purified by recrystallisation; yield 25% of theory. From this the octalin was regenerated by boiling with sodium methoxide in methyl alcohol. The yield from *cis*- is greater than that from *trans*- $\beta$ -decalols.

$\Delta^9$ -Octalin thus obtained has b.p. 194°/750 mm., 79°/14 mm.; m.p. –34°;  $\rho_4^{20}$  0.9170;  $n_D^{19.6}$  1.49963. It is characterised by forming a blue nitrosochloride, m.p. 92.5° (the blue colour, resembling copper sulphate, being given only by hydrocarbons having a double bond between two tertiary carbon atoms), and a dibromide, m.p. 163–164°.  $\Delta^9$ -Octalin is also obtained by dehydrating *cis*- or *trans*-2-cyclopentylcyclopentanol (Zelinski, Tiz, and Fatejev, Bor. 1926, 59 [B], 2580; Hückel *et al.*, Annalen, 1929, 477, 99) and by dehydrating 1- $\Delta^7$ -butenylcyclohexanol (Linstead *et al.*, J.C.S. 1937, 1136).

With ozone in light petroleum  $\Delta^9$ -octalin gives a stable ozonide, m.p. 168°; but in acetic acid solution it is oxidised by ozone to cyclodecane-1:6-dione and  $\delta$ -ketosebacic acid. With benzoyl peroxide it forms an oxide, b.p. 82–83°/12 mm., which on hydration gives decalin-9:10-diol, probably a mixture of *cis*- and *trans*-isomers since the melting-point of different fractions is between 84.5° and 92° (Hückel *et al.*, *l.c.*). Nametkin and Glagoleff (*l.c.*) gave the melting-point of the diol as 66–67°.

By oxidising  $\Delta^9$ -octalin with chromic and acetic acid Hückel and Naab obtained what they considered to be pure *trans*-decalin-9:10-diol, m.p. 96° (monoacetate, m.p. 132°), whilst Criegee, using osmium tetroxide as oxidising agent, obtained what he considered to be *cis*-decalin-9:10-diol, m.p. 89.5°, which depressed the melting-point of Hückel's product of benzoyl peroxide oxidation (Annalen, 1936, 522, 93).

The oxidation of  $\Delta^9$ -octalin by selenium dioxide was studied by Campbell and Harris (J. Amer. Chem. Soc. 1941, 63, 2721); in glacial acetic acid with 1 mol. of reagent,  $\Delta^9$ -1-octyl acetate is formed, and with 2 mol.,  $\Delta^9$ -1:5-dihydroxyoctalin diacetate, m.p. 122–123°; further oxidation of the former gives  $\Delta^9$ -octalin-1-one (semicarbazone, m.p. 241–242°) which Hückel and Naab had obtained by chromic acid oxidation of  $\Delta^9$ -octalin and considered to be  $\Delta^9$ -octalone; further oxidation of the diol diacetate gives  $\Delta^9$ -octalin-1:5-dione, m.p. 113–114°.

When hydrogenated in the presence of

platinum black in acetic acid solution,  $\Delta^9$ -octalin gives a mixture of *cis*- and *trans*-decalin in the ratio 2:1.

$\Delta^{10}$ -Octalin is obtained by thermal decomposition of the methyl xanthate ester of *trans*-decahydro- $\alpha$ -naphthol, m.p. 63°, forming 80% of the octalin product, the other 20% being *trans*- $\Delta^{10}$ -octalin. It has b.p. 196.5–198.5° and forms a bimolecular nitrosochloride, m.p. 127°. By ozonisation it gives mainly  $\gamma$ -2-ketocyclohexylbutyric acid.

2-Keto-10-methyl- $\Delta^{10}$ -octalin (2:4-dinitrophenylhydrazon, m.p. 169°) and 2-keto-8-methyl- $\Delta^{10}$ -octalin (2:4-dinitrophenylhydrazon, m.p. 172°) have been synthesised by R. Robinson, du Feu, and McQuillin (J.C.S. 1937, 53).

$\Delta^1$ -Octalins.—The *cis*- and *trans*-forms of  $\Delta^1$ -octalin do not appear to have been accurately characterised. *cis*- $\Delta^1$ -Octalin is present along with the  $\Delta^2$ -isomer in the octalin obtained by dehydrating *cis*- $\beta$ -decalol by heating with potassium hydrogen sulphate, and is formed by thermal decomposition of the methyl xanthate ester of *cis*- $\alpha$ -decalol, m.p. 93° (Hückel *et al.*, *l.c.*). *trans*- $\Delta^1$ -Octalin, may be formed, along with the  $\Delta^2$ -octalins, when mixed 2-chlorodecalins are heated with aniline (Borsche and Lange, Annalen, 1923, 434, 210).

The synthesis of some 1:2-dialkyl- $\Delta^1$ -octalins has been described by Nesty and Marvel (J. Amer. Chem. Soc. 1937, 59, 2662).

$\Delta^2$ -Octalins.—*cis*- $\Delta^2$ -Octalin, b.p. 72–73°/15 mm., is obtained from *cis*-2-chlorodecalin (Borsche and Lange, *l.c.*) and is characterised by a dibromide, m.p. 170°.

*trans*- $\Delta^2$ -Octalin is obtained when *trans*- $\beta$ -decalol, m.p. 75°, is dehydrated by heating with potassium hydrogen sulphate at 200°; it has m.p. –24°, b.p. 190–192°,  $\rho^{13}$  0.901,  $n_D$  1.491, and forms a dibromide, m.p. 85°. On oxidation it gives *trans*-cyclohexanediacetic acid. It was first prepared by Leroux (Ann. Chim. 1910, [viii], 21, 458) and its identity was established by Borsche and Lange, and by Hückel (*l.c.*) It is hydrogenated (platinum black in acetic acid) three times as fast as  $\Delta^9$ -octalin (Hückel *et al.*, *l.c.*).

An amine assumed to be 10-amino- $\Delta^{10}$ -octalin, m.p. –11°, has been described by Hückel and Blohm (Annalen, 1933, 502, 114).

## DECAHYDRONAPHTHALENES (DECALINS).

The formation of decalin by hydrogenation of naphthalene, its manufacture and the properties of the commercial product have already been described (p. 413c).

Decalin (decahydronaphthalene,  $C_{10}H_{18}$ ) exists in two stereoisomeric forms, *cis*- and *trans*- (see p. 414c) which differ appreciably in physical properties and in some of their chemical properties. The possibility of this kind of isomerism of decahydronaphthalene was deduced on theoretical grounds by Mohr (J. pr. Chem. 1918, [ii], 98, 321; Bor. 1922, 55 [B], 230) and the existence of the two forms was first reported by W. Hückel (Nach. K. Ges. Wiss. Göttingen, 1923, 43) who subsequently carried out most important work on the isomeric forms of decalin

and its derivatives. The two forms of decalin were obtained by fractional distillation of technical decalin, by reduction of the *cis*- and *trans*- $\beta$ -decalones by Clemmensen's method and from *cis*- and *trans*- $\beta$ -decalols by dehydrating these to octalins and reducing them catalytically. Which of the isomers has the *cis*- and which the *trans*-configuration was deduced partly on grounds of analogy with known cyclohexane derivatives (*cis*-forms generally have the higher boiling-point, density, and refractive index), and partly from their relationship to the *cis*- and *trans*-decalols and -decalones, for which there is independent chemical evidence of configuration (Hückel, *Annalen*, 1925, 441, 1).

Decalin is a colourless, steam-volatile liquid with an odour of menthol. The physical constants, including most recent determinations, are as follows:

M.p.: *cis*-,  $-45^{\circ}$ ; *trans*-,  $-33^{\circ}$  (Hückel, *ibid.* 1938, 533, 25).

M.p.: *cis*-,  $43.25^{\circ}$ ; *trans*-,  $-31.16^{\circ}$  (Seyer and Leslie, *J. Amer. Chem. Soc.* 1942, 64, 1912).

B.p.: *cis*-,  $193^{\circ}$ ; *trans*-,  $185^{\circ}$  (Hückel, 1925, *l.c.*).

B.p.: *cis*-,  $194.6^{\circ}$ ; *trans*-,  $185.4^{\circ}$  (Seyer and Leslie, *l.c.*).

Density: *cis*-,  $d_4^{20}$  0.893–0.898; *trans*-, 0.8709 (Hückel, 1925 and 1938, *l.c.*).

Refractive index: *cis*-,  $n_D^{20}$  1.480–1.482; *trans*-, 1.4696–1.4713 (Hückel, *l.c.*).

Critical temp: *cis*-,  $418$ – $419^{\circ}$ ; *trans*-,  $408$ – $408.5^{\circ}$  (Hückel, 1938, *l.c.*).

Viscosity, in antipoises: *cis*-,  $0^{\circ}$ , 5.620;  $10^{\circ}$ , 4.300;  $20^{\circ}$ , 3.381;  $100^{\circ}$ , 0.920; *trans*-,  $0^{\circ}$ , 3.233;  $10^{\circ}$ , 2.588;  $20^{\circ}$ , 2.128;  $100^{\circ}$ , 0.692 (Seyer and Leslie, *l.c.*).

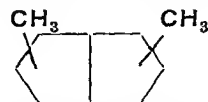
Mol. heats of combustion: *cis*-, 1499.9 kg.-cal.; *trans*-, 1496.9, kg.-cal. (Roth and Lassé, *Annalen*, 1925, 441, 48); *trans*-, 1493.7 kg.-cal. (Hückel, 1938, *l.c.*).

It follows from the discovery of the two forms of decalin in 1923 that the earlier work on decalin and its derivatives, especially that concerning physical constants, loses much of its value. References to earlier work will be found in Hückel's papers already quoted. It appears from results quoted by Willstätter and Seitz that the product of catalytic hydrogenation of naphthalene using platinum is almost pure *cis*-isomer (Ber. 1924, 57 [B], 683) although Hückel considered it to contain 10% of the *trans*-form. Linstead *et al.* (*J. Amer. Chem. Soc.* 1942, 64, 1985) have offered a mechanical explanation for the observation that catalytic hydrogenation of polycyclic hydrocarbons at a low temperature gives *cis*-compounds. Yet it is to be noted that Hückel obtained a mixture of *cis*- and *trans*-decalin (ratio 2:1) by hydrogenating  $\Delta^9$ -octalin using platinum black in acetic acid as catalyst (*Annalen*, 1929, 474, 121). The dehydrogenation of decalin by platinum on different carriers at  $200$ – $350^{\circ}$  has been studied by Zelinski and Balandin (*Z. physikal. Chem.* 1927, 126, 267; *Bull. Acad. Sci. U.R.S.S.* 1929, 1, 29).

*Properties*.—Decalin is comparatively stable

towards oxidation but according to Castiglioni (*Gazzetta*, 1934, 64, 465) undergoes autoxidation in air in the presence of light, especially ultra-violet. Acid permanganate oxidises it to *phthalic acid*. Its oxidation by ozone has been studied by Durland and Adkins (*J. Amer. Chem. Soc.* 1939, 61, 430); the *cis*-form is more readily attacked than the *trans*-, giving 9-hydroxy-*cis*-decalin, some  $\Delta^9$ -octalin, and a little *cis*- $\alpha$ -decalone. The *trans*-form gave a 28% yield of 9-hydroxy-*trans*-decalin, with  $\Delta^9$ -octalin and some *trans*- $\alpha$ -decalone. Oxidation of *trans*-decalin with selenium dioxide gives 2.3- (or 1:2-) *diketo-trans*-decalin, whilst Caro's acid gives a *peroxide*, m.p.  $174^{\circ}$  (Rao and Kuppuswamy, *J. Annamalai Univ.* 1937, 7, 22).

Since decalin is stable to cold concentrated sulphuric acid, and even to weak oleum, these reagents can be used to purify it from less saturated hydrocarbons such as tetralin. It is also insoluble in liquid sulphur dioxide, which can be used for the same purpose (Tetralin G.m.b.H., G.P. 310781). According to Prokopetz, when decalin is shaken with 20% oleum, the *cis*-isomer alone is oxidised, leaving the *trans*-unaffected (*J. Appl. Chem. Russ.* 1935, 8, 1214). Chlorine attacks decalin in the cold forming chloro derivatives (*v.i.*); bromine is without action in the cold, but at higher temperatures has a dehydrogenating action, and bromonaphthalenes are formed (Leroux, *Ann. Chim.* 1910, [viii], 21, 460). Attack by bromine takes place very readily in the presence of aluminium bromide, and the curious result was observed by Zelinsky and Turova-Pollak (Ber. 1929, 62 [B], 1658) that, using the requisite proportion of bromine, *cis*- and *trans*-decalin gave two different hexabromonaphthalenes, m.p.  $312^{\circ}$  and  $269^{\circ}$  respectively. Since the former only is obtained by direct bromination of naphthalene, it cannot be assumed that dehydrogenation of decalin precedes bromination. The same authors found that *cis*-, but not *trans*-decalin forms a molecular compound with aluminium bromide, and that this reagent changes the *cis*- into the *trans*-form, other hydrocarbons being formed at the same time (*ibid.* 1925, 58 [B], 1292). Amongst the hydrocarbons formed by the action of aluminium bromide and of aluminium chloride on decalin at  $130^{\circ}$  is an isomeric hydrocarbon, a dimethyl-0:3:3-bicyclooctane,



in which the positions of the methyl groups are uncertain (*J. Appl. Chem. Russia*, 1934, 7, 753; Jones and Linstead, *J.C.S.* 1936, 616).

#### CHLORODECALINS.

Mono- and di-chlorodecalins, liquids, have been obtained by chlorinating decalin, but it is doubtful whether individual compounds have yet been isolated, except possibly the 2-chloro-*cis*-decalin, b.p.  $110$ – $112^{\circ}$ /15 mm. obtained by Borsche and Lange from *cis*- $\beta$ -decalol, m.p.  $104^{\circ}$ ; individual compounds should, however, be obtainable now that all the isomeric decalols

have been characterised by Hückel (*see* Leroux, *Ann. Chim.* 1910, [viii], 21, 460; Borsche and Lange, *Annalen*, 1923, 434, 219; Zelinski and Gavedovskaja, *Ber.* 1924, 57 [B], 2062; Gysin, *Helv. Chim. Acta*, 1926, 9, 59).

#### BROMODECALINS.

The chemistry of the brominated decalins is also in an incomplete state. They have been obtained from the octalins by addition of hydrogen bromide or bromine. A 9-bromo-decalin, m.p. 29–30°, was obtained by Clemons and Ormston by the addition of hydrogen bromide at 0° to  $\Delta^9$ -octalin; its configuration, *cis*- or *trans*-, is unknown (*J.C.S.* 1932, 1778). A 9:10-dibromodecalin, m.p. 163–164°, is formed by addition of bromine to the same octalin (Hückel *et al.*, *Annalen*, 1929, 474, 121). Leroux (*l.c.*) described a 1:2-dibromodecalin, m.p. 143°. 2:3-Dibromo-*trans*-decalin, m.p. 85°, has been obtained by Leroux, by Borsche and Lange, and by Hückel; the two bromine atoms are probably in *cis*-configuration. Leroux also described a second 2:3-dibromodecalin, m.p. 41°, which did not give a *cis*-glycol on hydrolysis (*cf.* Ganapathi, *Ber.* 1939, 72 [B], 1381).

#### NITRODECALINS.

The nitration of decalin has been studied by Nametkin and Madaev-Sitschov (*ibid.* 1926, 59 [B], 370) and by Hückel and Blohm (*Annalen*, 1933, 502, 114). The former used technical decalin which is nitrated by prolonged boiling with nitric acid,  $\rho$  1.20, giving mainly 9-nitro-decalin, b.p. 96–97°/2 mm., insoluble in alcoholic potassium hydroxide, a little 1-nitrodecalin, b.p. 108–109°/14 mm., soluble, and some 9:10-dinitrodecalin, m.p. 164° (decomp.). Hückel and Blohm studied the nitration of pure *trans*-decalin as well as a mixture of 65% *cis*- and 35% *trans*-. The *trans*-isomer gave almost entirely 9-nitro-*trans*-decalin, m.p. 24°; the same isomer is the main product of nitrating the mixture, some Walden inversion occurring. The nitro-*cis*-decalin could not be obtained pure, but pure 9-amine was obtained by reducing the impure material (*v.i.*). By reducing 9-nitro-*trans*-decalin with aluminium amalgam, 9-nitroso-*trans*-decalin, m.p. –16°, was obtained. It forms blue crystals (*cf.*  $\Delta^9$ -octalin nitroso-chloride), but also exists in a colourless bimolecular form, m.p. 100°.

#### AMINO AND HYDROXY DERIVATIVES.

Aminodecalins (*decalylamines*) were first prepared by Leroux (*Ann. Chim.* 1910, [viii], 21, 530) by reducing the oximes of  $\alpha$ - and  $\beta$ -decalones with sodium and alcohol. He obtained them as liquids of unpleasant odour, having the properties of strong bases.  $\beta$ -Naphthylamine can be reduced to decahydro- $\beta$ -naphthylamine by hydrogen in the presence of nickel or nickel chromite using conditions ranging at first from 175–225°/1,000–2,000 lb. per sq. in. and subsequently 250–300°/2,000–3,000 lb. per sq. in.; as a by-product di-decahydro- $\beta$ -naphthylamine is obtained (*I.C.I.*, B.P. 506928; U.S.P. 2127377). All detailed knowledge of  $\alpha$ - and  $\beta$ -decalylamines is due, however, to the work of W. Hückel and his school.

Stereochemical considerations show that both *cis*- and *trans*-decalin should give rise to two different  $\alpha$ -mono-substituted derivatives; thus there should be four different  $\alpha$ -decalylamines, each of which contains asymmetric carbon atoms and should be resolvable into optical isomers. Ignoring optical isomers for the present, four  $\alpha$ -decalylamines, four  $\beta$ -decalylamines, four  $\alpha$ -decalols, and four  $\beta$ -decalols should be possible. When, however, the amino- or hydroxyl-group is attached to the 9 (=10) carbon atom, only two isomers are possible. These theoretical considerations have been completely confirmed by Hückel. He has been able to correlate the amino derivatives with the corresponding hydroxy derivatives, but it has not yet been possible to establish the configuration of the pairs of compounds such as the two *cis*- $\alpha$ -decalylamines. For purposes of nomenclature these are designated *cis*- $\alpha$ -decalylamine-I and *cis*- $\alpha$ -decalylamine-II, and so on. The complete series of decalylamines and decalols are given in the following Tables (*see* Hückel, *Annalen*, 1938, 533, 1; Hückel *et al.*, *ibid.* 1933, 502, 99) which include melting-points of characteristic derivatives.

#### $\alpha$ - AND $\beta$ -DECALYLAMINES.

Designation.	M.p.	Benzoyl derivative, m.p.	Acetyl derivative, m.p.
<i>cis</i> - $\alpha$ -Amlne-I	8°	206°	181°
<i>cis</i> - $\alpha$ -Amlne-II	–2°	193°	141°
<i>trans</i> - $\alpha$ -Amlne-I	–18°	112°	130°
<i>trans</i> - $\alpha$ -Amlne-II	–1°	195°	182°
<i>cis</i> - $\beta$ -Amlne-I	14°	204°	153°
<i>cis</i> - $\beta$ -Amlne-II	ca. 20°	128°	88°
<i>trans</i> - $\beta$ -Amlne-I	–47°	177°	130°
<i>trans</i> - $\beta$ -Amlne-II	15°	176–177°	163°

#### $\alpha$ - AND $\beta$ -DECALOLS.

Designation.	M.p.	Acid phthalate, m.p.	Acid succinate, m.p.
<i>cis</i> - $\alpha$ -Decalol-I	93°	176°	66°
<i>cis</i> - $\alpha$ -Decalol-II	55°	142°	54°
<i>trans</i> - $\alpha$ -Decalol-I	49°	121°	107°
<i>trans</i> - $\alpha$ -Decalol-II	63°	168°	85°
<i>cis</i> - $\beta$ -Decalol-I	105°	116°	81°
<i>cis</i> - $\beta$ -Decalol-II	18°, 31°	153°	59°
<i>trans</i> - $\beta$ -Decalol-I	53°	107–180°	61°
<i>trans</i> - $\beta$ -Decalol-II	75°	180°	81°

The amines and alcohols are obtained respectively by acid or alkaline reduction of the corresponding ketoximes and of the ketones themselves (*cis*- and *trans*- $\alpha$ - and  $\beta$ -decalones, *v.i.*). The products designated I are obtained predominantly by reduction under acid conditions, those designated II under alkaline conditions. In the  $\alpha$ -series a uniform product is generally obtained by reduction under one or other set of conditions, but in the  $\beta$ -series a mixture of products is more often formed.

It is interesting to note that by treatment with nitrous acid both amines I and II of the *trans*-series give decalols II, the former undergoing Walden inversion; and whereas amines II give a quantitative yield of decalol, amines I give



only 30% of decalol with 70% of octalin. In the *cis*-series, however, the  $\beta$ -amines and not the  $\alpha$ -amines undergo Walden inversion and there is no relation between occurrence of inversion and production of octalin.

*cis*- $\beta$ -Decalylamine I, m.p. 15°, after careful purification, has been resolved into *d*- and *l*-forms through the *d*-camphorsulphonate. The *d*- and *l*-amines had m.p. 30-5°, benzoyl derivative, m.p. 205°, acetyl, m.p. 173°; the hydrochlorides in water gave  $[\alpha]_D^{25} \pm 15.4^\circ$  (Hückel and Kühn, Ber. 1937, 70 [B]. 2479). (For further information on the  $\alpha$ - and  $\beta$ -decalylamines, see Hückel *et al.*, Annalen, 1925, 441, 1: 1927, 451, 109; 1933, 502, 99: Ber. 1941, 74 [B]. 57).

The two 9-aminodecalins have been obtained by reduction of the 9-nitrodecalins; 9-amino-*trans*-decalin has m.p. -25°, acetyl, m.p. 183°, benzoyl, m.p. 148-149°; 9-amino-*cis*-decalin, m.p. -13°, acetyl, m.p. 127°, benzoyl, m.p. 147°. The latter was also obtained by reducing 9-nitroso-10-chlorodecalin (Hückel and Blohm, Annalen, 1933, 502, 114). The 9-aminodecalins do not undergo inversion when treated with nitrous acid to form 9-decalols, but much octalin is formed (*ibid.* 1933, 533, 1).

$\alpha$ -Decalols.—The hydrogenation of  $\alpha$ -naphthol under pressure in the presence of nickel oxide (225-230°, 168-172 atm.) was carried out in 1907 by Ipatieff (Ber. 1907, 40, 1237) who obtained a small yield of decahydro- $\alpha$ -naphthol, m.p. 57-59°. Later Leroux found that  $\alpha$ -naphthol could be hydrogenated with difficulty to a decahydro-compound in the vapour phase in the presence of reduced nickel: the reaction is carried out in two stages, the first at 170° and the second at 130°: the catalyst must be highly active, but if too active it causes dehydration to octalin. Leroux's product had m.p. 62°, b.p. 109°/14 mm.; both this and the material obtained by Ipatieff must have been *trans*- $\alpha$ -decalol-II.

According to English and Cavagliari, hydrogenation of  $\alpha$ -naphthol by Adams method gives mainly *trans*- $\alpha$ -decalol (J. Amer. Chem. Soc. 1943, 65, 1085).

The conditions under which the isomeric  $\alpha$ -decalols are formed are as follows. They can be separated by fractionation of their hydrogen phthalates, hydrogen succinates, or *p*-nitrobenzenesulphonates (see Hückel *et al.*, Annalen, 1925, 441, 1: 1930, 477, 150: 1933, 502, 99).

*cis*- $\alpha$ -Decalol-I, m.p. 93°, is formed almost exclusively by hydrogenating *cr*- $\beta$ -tetralol in the presence of platinum and acetic acid, and in good yield, with some *trans*- $\alpha$ -decalol-I, using colloidal platinum (Skita). Hydrogenation of  $\alpha$ -naphthol by the Skita method gives a small yield with much decalin and other products.

*cis*- $\alpha$ -Decalol-II, m.p. 55°, is obtained from *cis*- $\alpha$ -decalylamine-II.

*trans*- $\alpha$ -Decalol-I, m.p. 49°, is formed, as already indicated, by hydrogenating  $\alpha$ -naphthol under pressure with a nickel catalyst. At the same time a smaller quantity of *trans*- $\alpha$ -decalol-II is formed, the ratio being 3-4:1.

*trans*- $\alpha$ -Decalol-II, m.p. 63°, is formed as above, and better by Skita hydrogenation of *trans*- $\alpha$ -decalone.

Transformation of *cis*- $\alpha$ -decalol-I and *trans*- $\alpha$ -decalol-I to *trans*- $\alpha$ -decalol-II is said to occur when the former are heated at about 150° with sodium in xylene, using slightly more than enough sodium to form the alkoxide (Hückel and Naab, Ber. 1931, 64 [B]. 2137).

$\beta$ -Decalols.—When Leroux hydrogenated  $\beta$ -naphthol as described for  $\alpha$ -naphthol, he obtained a decahydro derivative, m.p. 75°, b.p. 238°; whilst Ipatieff, by his method, obtained a product of peppermint-like odour, m.p. 99-103°, which was later shown by Mascarelli (Atti R. Acad. Lincei, 1911, [r]. 20, ii, 223: Mascarelli and Recusani, Gazzetta, 1912, 42, ii, 35) to be a mixture of two isomers, m.p. 75° and 103°. That these were derived respectively from *cis*- and *trans*-decalin was shown by Hückel by oxidising them to known derivatives of *cis*- and *trans*-cyclohexane and by establishing their relation to *cis*- and *trans*- $\beta$ -decalones. The existence of the four isomeric  $\beta$ -decalols was established by Hückel in 1926 (Annalen, 1927, 451, 109). Zelinski and Turova-Pollak had isolated three  $\beta$ -decalols from technical decalol made by Poulenc Frères, but Hückel isolated all four isomers from a large sample of technical decalol (cf. J. D. Riedel, A.-G., G.P. 485715, 1926; this firm has a patent, G.P. 405664, for hydrogenating *cr*- $\beta$ -tetralol in the presence of nickel at 180° in tetralin solution to  $\beta$ -decalol). According to Hückel, hydrogenation of *cr*- or *cr*- $\beta$ -tetralol in the presence of platinum black and acetic acid gives *cis*- $\beta$ -decalol-I, m.p. 103°; colloidal platinum (Skita) produces decalin and a mixture of decalols containing much of the same isomer, some *trans*- $\beta$ -decalol-II, m.p. 75°, and more of *cis*- $\beta$ -decalol-II, m.p. 18°.

*cis*- $\beta$ -Decalol-I, m.p. 103°, is obtained as stated above, also by sodium reduction of *cis*- $\beta$ -decalone and from the *cis*- $\beta$ -amine-I (Hückel *et al.*, Annalen, 1925, 441, 1). It is practically odourless: its phenylurethane has m.p. 134°.

*cis*- $\beta$ -Decalol-II, m.p. 18°, has an intense sweet smell. It is produced along with the other *cis*-form by sodium reduction of *cis*- $\beta$ -decalone. Its phenylurethane has m.p. 102°.

*trans*- $\beta$ -Decalol-I, m.p. 53°, is formed, along with the other *trans*-isomer by hydrogenation (Skita or Willstätter) of *trans*- $\beta$ -decalone. It has an intense odour of menthol. Its phenylurethane has m.p. 99° and it is best purified through its oxalate, m.p. 143°.

*trans*- $\beta$ -Decalol-II, m.p. 75°, is obtained as mentioned above, and also from the action of nitrous acid on both forms of *trans*- $\beta$ -decalylamine.

When heated with sodium and xylene both *cis*- $\beta$ -decalols give a mixture containing 80% of *cis*- $\beta$ -decalol-I and 20% of *cis*- $\beta$ -decalol-II; the *trans*- $\beta$ -decalol-I is converted into *trans*- $\beta$ -decalol-II (Hückel and Naab, *loc. cit.*).

The optically active forms of *cis*- $\beta$ -decalylamine-I referred to above gave on treatment with nitrous acid optically active forms of *cis*- $\beta$ -decalol-II, m.p. 38°, forming a racemic compound, m.p. 31°. The phthalate of the (-)-decalol had a negative rotation.

9-Hydroxydecalins.—These are obtained by the action of nitrous acid on the 9-amines. 9-Hydroxy-*cis*-decalin has m.p. 63°; 9-hydroxy-



*trans-decalin*, m.p. 54°. 9-Amino-10-hydroxy-decalin has m.p. 103° (Hückel and Blohm, *ibid.* 1933, 502, 114).

### DIHYDROXYDECALINS.

2:3-Dihydroxydecalins. — Two isomeric 2:3-dihydroxydecalins were obtained by Leroux from 2:3-dibromodecalin, m.p. 85°, which was prepared from  $\Delta^2$ -octalin and bromine. The first, obtained by the action of aqueous potash on the dibromo-compound, had m.p. 160°; in this compound the two hydroxyl groups must have *cis*-configuration, since it is also obtained from octalin-2:3-oxide (liquid, b.p. 225°) which is formed by the action of cold alcoholic potassium hydroxide on octalin-2:3-iodohydrin, m.p. 70° (Ann. Chim. 1910, [viii], 21, 495). According to Ganapathi (Ber. 1939, 72 [B], 1381) this glycol is *cis*-2:3-dihydroxy-*trans*-decalin, and its true m.p. is 166°. This glycol (m.p. 168°) has also been obtained by Lehmann and Krätschell by dismutation of 3-hydroxy-*trans*- $\beta$ -decalone (*ibid.* 1935, 68 [B], 360). Its *bisphenylurethane* has m.p. 195° (Leroux). The second glycol, *trans*-2:3-dihydroxy-*trans*-decalin, m.p. 141°, was obtained by the action of silver acetate in acetic acid on the same dibromo-compound; its *bisphenylurethane* has m.p. 121°. It is also formed by reduction of 2:3-diketo-*trans*-decalin with sodium amalgam (Ganapathi), and by reduction of a 3-hydroxy-*trans*- $\beta$ -decalone of m.p. 134° (Lehmann and Krätschell, *loc. cit.*). A third glycol, m.p. 125°, obtained along with the second, was considered by Leroux to be a molecular compound of the first two, but Ganapathi, who obtained it, m.p. 128–129°, by reduction of 2:3-diketo-*trans*-decalin with aluminium amalgam in moist ether, regards it as a second *cis*-2:3-dihydroxy-*cis*-decalin.

1:5-Dihydroxydecalin. — By hydrogenation of 1:5-dihydroxynaphthalene over Raney nickel at 100–150°/120 atm., Robinson and Hudson obtained mixed decalin-1:5-diols m.p. 130–150°, with indications of a definite compound, m.p. 159–161° (J.C.S. 1942, 691). A different decalin-1:5-diol was obtained by Campbell and Harris (J. Amer. Chem. Soc. 1941, 63, 2721) by hydrogenation (Adams platinum) of octalin-1:5-diol diacetate.

9:10-Dihydroxydecalin. — See decalin-9:10-diol (p. 433b).

### DECAHYDRO- $\beta$ -NAPHTHALDEHYDE.

This substance has been prepared from  $\beta$ -decalone by Darzen's reaction. It is a liquid, b.p. 100–102°/4 mm., with an odour of ambergris and is claimed as a perfume (I.G., B.P. 372013).

### DECALINCARBOXYLIC ACIDS.

By complete hydrogenation of  $\alpha$ - and  $\beta$ -naphthoic acids, in the presence of platinum oxide Ranedo and Léon obtained *decalin-1-carboxylic acid*, m.p. 127° (chloride, b.p. 200°/120 mm., *amide*, m.p. 198–199°) and *decalin-2-carboxylic acid*, m.p. 72–76° (chloride, b.p. 210°/180 mm., *amide*, m.p. 145°) (Anal. Fis. Quim. 1927, 25, 421). Borsche and Lange (Annalen, 1923, 434, 219) obtained a mixture of acids by treating the Grignard compounds from 2-chlorodecalin

with carbon dioxide, and separated two acids which they called *cis*-decalin-2-carboxylic acid, a resin (*amide*, m.p. 165–166°), and *trans*-decalin-2-carboxylic acid, m.p. 103° (*amide*, m.p. 155–158°). There should, according to stereochemical theory, be four different decalin-2-carboxylic acids, and Kay and Stuart (J.C.S. 1926, 3038) obtained what they consider to be four different amides. Two were obtained by fractional crystallisation of the amides of the acid, m.p. 65–75°, obtained by reducing  $\alpha$ -tetrahydro- $\beta$ -naphthoic acid with sodium and amyl alcohol; the other two from the amide of the acid, m.p. 80–90°, obtained by reducing with sodium and ethyl alcohol. The first two amides had m.p. 195–196° and 171–174°; the other two, m.p. 169–171° and 139–140°.

A mixture of stereoisomeric decalin-1-carboxylic acids was obtained by Long and Burger (J. Org. Chem. 1941, 6, 852) by hydrogenating 6-methoxy-1-naphthoic acid, the methoxyl group being eliminated. 1-Hydroxydecalin-2-carboxylic acid, m.p. 198°, was prepared by Hückel and Goth by hydrogenating ethyl 1-keto-1:2:3:4-tetrahydronaphthalene-2-carboxylate, and hydrolysing the ester. Some decalin-2-carboxylate was formed at the same time (Ber. 1924, 57 [B], 1285).

A decalin-9:10-dicarboxylic acid (anhydride, m.p. 96°, *imide*, m.p. 188–189°) has been obtained by condensing  $\Delta^1$ -tetrahydrophthalic acid with butadiene and hydrogenating the so-obtained octalin-9:10-dicarboxylic acid, the anhydride of which had m.p. 68° (Brigl and Herrmann, *ibid.* 1938, 71, [B], 2280).

### DECALONES.

The decalones have already been referred to in connection with the decalols, which are obtained from them by hydrogenation, and the decalylamines, formed by hydrogenation of the decaloximes. There are four possible monoketodecalins, namely the  $\alpha$ - and  $\beta$ -decalones derived from both *cis* and *trans*-decalin. These four ketones were characterised and their configurations established with reasonable certainty by Hückel in his work on the stereochemistry of decahydronaphthalene (Annalen, 1925, 441, 1). The complete line of argument is too long to give here, but it may be mentioned that oxidation of one of the  $\alpha$ -decalones with nitric acid gives *cis*-cyclohexano-1-propionic-2-carboxylic acid, m.p. 103°, whilst similar oxidation of the other gives the *trans*-acid, m.p. 143°, and that *cis*- $\beta$ -decalone was synthesised by cyclisation of *cis*-cyclohexano-1-acetic-2-propionic acid.

The decalones are prepared by oxidation of the corresponding decalols with chromic acid in acetic acid solution. They are oils or low melting solids; the  $\alpha$ -decalones have odours resembling menthol; the  $\beta$ -ketones have a less agreeable smell.

The decalones have acquired some importance as intermediates in the synthesis of substances related to the sterols.

$\alpha$ -Decalones. — Mixed *cis*- and *trans*- $\alpha$ -decalones, obtained by oxidation of mixed  $\alpha$ -decalols, can be separated by fractional crystallisation of the somicarbazones (English and

Cavaglieri, J. Amer. Chem. Soc. 1943, 65, 1085). According to Hückel (l.c.), the *cis*-form is changed to *trans*- by acid and alkaline reagents and by distillation at ordinary pressure, but English and Cavaglieri could not confirm these observations. According to Hückel, condensation of *cis*- $\alpha$ -decalone with oxalic ester and subsequent degradation back to the ketone gives *trans*- $\alpha$ -decalone; and attempts to make the oxime of the *cis*-ketone only give *trans*- $\alpha$ -decalone oxime.

*cis*- $\alpha$ -Decalone has m.p. 2°, b.p. 126°/20 mm.,  $\rho_4^{20}$  1.008,  $n_D^{20}$  1.49364; *semicarbazone*, m.p. 220–221° (decomp.), (Hückel, l.c.).

*trans*- $\alpha$ -Decalone has m.p. 33°,  $\rho_4^{20}$  0.986,  $n_D^{23}$  1.48372; *semicarbazone*, m.p. 229–230°; *benzylidene* derivative, m.p. 91°, *oxime*, m.p. 168° (Hückel, l.c.).

Methylation of 2-benzylidene-1-decalones gives the 9-methyl derivatives, whence are obtained 9-methyl-*cis*-1-decalone (*semicarbazone*, m.p. 226–227°) and 9-methyl-*trans*-1-decalone (*semicarbazone*, m.p. 219–220°), both liquids of camphor-like odour (Johnson, J. Amer. Chem. Soc. 1943, 65, 1317).

$\beta$ -Decalones.—A technical  $\beta$ -decalone from J. Riedel examined by Wallach and Weissenborn (Annalen, 1924, 437, 161) was found to be a mixture of two products, and Hückel (l.c.) found a technical product of unnamed origin to consist of 60% *trans*- and 40% *cis*-decalone. The heats of combustion of the *cis*- and *trans*- $\beta$ -decalones are equal, 1,400.2 kg.-cal. per mol. (Roth and Lassé, *ibid.* 1925, 441, 48).

*cis*- $\beta$ -Decalone has m.p. –14°, b.p. 247°/755 mm.,  $\rho_4^{21}$  1.0039,  $n_D^{21}$  1.49180; *semicarbazone*, m.p. 182–183° (decomp.); *oxime*, oil, b.p. 161–165°/16 mm.

According to Cook and Lawrence (J.C.S. 1937, 824), chlorination gives 3-chloro-*cis*-2-decalone, m.p. 107–108°; methylation of *cis*-2-decalone takes place in the 3-position, and condensation with ethyl oxalate and sodium chloride gives *ethyl cis*-2-decalone-3-glyoxylate, b.p. 130°/0.7 mm.

*trans*- $\beta$ -Decalone has m.p. 6°, b.p. 241°/755 mm.,  $\rho_4^{20}$  0.975,  $n_D^{19}$  1.48088; *semicarbazone*, m.p. 192–193° (decomp.); *oxime*, m.p. 76°.

Chlorination of *trans*- $\beta$ -decalone gives 3-chloro-*trans*-2-decalone, m.p. 92°, and a *dichloro* derivative, m.p. 137°. The former is changed by hot sodium hydroxide into 3-hydroxy-*trans*-2-decalone which exists in two forms, m.p. 84° and 134° (Lehmann and Krätschell, Ber. 1934, 67 [B], 1867).

The cyanohydrin of *trans*- $\beta$ -decalone condenses with aromatic amines to give 2-cyano-2-aryl-amino-*trans*-decalins, which exist in two forms (Desai, Hunter, and Hussain, J.C.S. 1936, 1675).

When *trans*- $\beta$ -decalone is heated with selenium at 260° a small yield of  $\beta$ -naphthol is obtained (Ruzicka, Helv. Chim. Acta, 1936, 19, 419); heated with selenium dioxide in boiling ethyl alcohol it is oxidised to 2:3-diketodecalin, m.p. 99–100°, giving a *dioxime*, m.p. 229° (Ganapathi,

J. Indian Chem. Soc. 1938, 15, 407). The diketone was reduced to the 3-hydroxy-2-decalone, m.p. 134°, and 2:3-dihydroxydecalin, m.p. 141°.

Wallach and Weissenborn also obtained a 2:3-diketodecalin by brominating mixed *cis*- and *trans*- $\beta$ -decalone and hydrolysing the product with alkali. This substance, m.p. 88–89°, has phenolic properties; they called it a “diosphenol” and gave it the structure of 2-hydroxy-3-keto- $\Delta^1$ -octalin. It formed a *dioxime*, m.p. 196–197°. A small quantity of an isomeric diketone, m.p. 99–100° (cf. Ruzicka's compound) was also isolated (Annalen, 1924, 437, 163).

1:3-Diketo-*trans*-decahydronaphthalene was synthesised by Kon and Khuda (J.C.S. 1926, 3071) and by Chuang and Tien (Ber. 1936, 69 [B], 25) from 1-acetylcyclo- $\Delta^1$ -hexene and ethyl sodiomalonate. The latter authors give m.p. 152–153° (2-benzylidene derivative, m.p. 229°). They noted that the *trans*-isomer was formed when 1:3-diketodecalin-4-carboxylic ester was boiled with 20% alcoholic potash, but by the action of a more dilute reagent at 15–20°, 1:3-diketo-*cis*-decalin, m.p. 124–125°, was formed.

Two decalin-1:5-diones, m.p. 68–72° and 164–167°, respectively, were obtained by Robinson and Hudson by oxidising (chromic-acetic acid) the decalin-1:5-diol obtained by catalytic reduction of 1:6-dihydroxynaphthalene (J.C.S. 1942, 691).

#### HOMOLOGUES OF DECALIN.

It would be beyond the scope of this article to give a full account of what is known of the homologues of decalin and its derivatives. Alkyl-naphthalenes can be hydrogenated to alkyldecalins, but comparatively little has been done yet to isolate the stereoisomers. It may be noted that some sesquiterpenes are closely related to alkylated decalins (cf. Ruzicka *et al.*, Helv. Chim. Acta, 1931, 14, 1131, 1151; Annalen, 1927, 453, 62). In recent years use has been made of alkylated decalols and decalones for synthetic purposes; for instance, numerous papers by R. Robinson and his collaborators on the synthesis of substances related to the sterols may be found in the Journal of the Chemical Society. The following references are given as a guide to some of the literature:

1-Methyl-decalols and -decalones, Robinson and Weygand, J.C.S. 1941, 388; English and Cavaglieri, J. Amer. Chem. Soc. 1943, 65, 1085. 2-Methyldecalone, Cook and Lawrence, J.C.S. 1937, 817; 9-Methyldecalones, Woodward, J. Amer. Chem. Soc. 1940, 62, 1211; Johnson, *ibid.* 1943, 65, 1317; Plentl and Bogert, J. Org. Chem. 1941, 6, 669.

The catalytic dehydrogenation of methyl-decalins has been studied by Linstead and collaborators. When a methyl group is present in the 9-position, no dehydrogenation occurs at 200°, but at 300° the methyl group is either eliminated or migrates to the  $\alpha$ -position, according to the catalyst used (J.C.S. 1937, 1146).

1- and 2-Ethyldecalins, b.p. 222° and 221°, respectively, have been obtained by hydrogenating the ethyl-naphthalenes in the presence of nickel at 160° (Lévy, Compt. rend. 1931, 192, 1397; 193, 174).

E. H. R.

NAPHTHANIL (*v.* Vol. IV, 231a).  
 NAPHTHAPHENANTHRIDINE AL-  
 KALOIDS (*v.* Vol. II, 529b).  
 NAPHTHAPHENAZINE (*v.* Vol. I, 565c).  
 NAPHTHASTYRIL (*v.* Vol. I, 426a).  
 "NAPHTHAZOLE" (*v.* Vol. IV, 231a).

**NAPHTHENIC ACIDS.** The term "naphthenic acids" is employed to denote those carboxylic acids which occur in petroleum, not including, however, the known fatty acids (*e.g.*, palmitic, stearic) which have been found in small quantities in certain crudes. Thus the terms "naphthenic acids" and "petroleum acids" are very nearly synonymous, the latter however including also *all* carboxylic acids found in petroleum. This distinction is however largely academic, since, in commercial naphthenic acid mixtures, traces of fatty acids will be present, if they occur in the crude whence the naphthenic acid mixture is derived.

Hitherto acids obtained from petroleum by artificial oxidation methods have not generally been included in the term "naphthenic acids"; whether they should be is a moot question. The term "polynaphthenic acids" (or "asphaltogenic acids") has been used in this connection, but the structures of such products are as yet undetermined.

**Occurrence.**—Naphthenic acids were first discovered, in 1874, in petroleum of Russian and of Roumanian origin, the name itself dating from 1883. Since then, investigation has shown that they are present, in lesser or greater amount, in practically all crudes. The content of naphthenic acids may vary from below 0.1% to considerably over 2%. As a general rule the crudes of a paraffinic type have a lower content of acids than crudes belonging to the naphthenic and asphaltic groups. Thus, Pennsylvania crudes usually have naphthenic acid contents of about 0.03%, whilst certain crudes from California have been examined in which as much as 3% is found. These acid contents correspond to approximate acidities of the crude oil of from 0.05 to 6.0 mg. KOH/g.

**Distribution in Crude Oil.**—This is not uniform, and in practically all oils investigated the concentration of acids rises with boiling-point, to reach a maximum in the kerosene-spindle oil range (*i.e.*, b.p. ca. 200–300°), thereafter falling again. Curves showing the distribution of naphthenic acids in various crudes with respect to the boiling-point of the fractions are given by Schmi z (Bull. Assoc. franç. Tech. Pétrole, 1938, Nov., p. 93). There is considerable evidence that a certain amount of naphthenic acids is produced by the breakdown of oxygenated bodies on the distillation of crude oil, although the extraction of naphthenic acids direct from crude oil has disposed of the earlier theory that the bulk, if not all, of the naphthenic acids were thus formed. That some acids are nevertheless produced on distillation has been proved by investigations on crude oil that has been, experimentally, completely neutralised, and which, however, yields acid distillates.

**Recovery.**—The recovery of naphthenic acids, on a laboratory scale, is performed by the extraction of the crude oil, or petroleum fractions under investigation, with alcoholic potash, pro-

ferably by boiling under reflux; the alcoholic solution is then diluted with water, and extracted with ether, in order to remove any hydrocarbon material dissolved in the alkali naphthenate solution. After removal of the ethereal extract, the solution is acidified with sulphuric acid, causing the separation of naphthenic acids, which are then extracted by light petroleum, freed from the latter by evaporation, and weighed.

Identification of the extracted material may be carried out by the Charitschkov reaction (*J. Russ. Phys. Chem. Soc.* 1897, 29, 691), which consists in neutralising the material with caustic soda, adding copper sulphate solution, and extracting with benzene. If naphthenic acids are present, they form, under these conditions, a copper salt which is soluble in benzene, and which may be recognised by its intense green colour. This reaction forms the basis of a method for the determination of naphthenic acids in soda-neutralised oils ("Standard Methods," 7th ed., Institute of Petroleum, London, 1946, p. 258). It should be noted that a similar reaction may also be given by certain fatty acids.

On an industrial scale, the acids are recovered either by the alkaline treatment of crude oil, or of its distillates, or else by distilling the reduced crude over alkali.

The caustic soda extraction of crude oils is of limited applicability, since it is only possible in the case of relatively light crudes, which will separate easily from the aqueous layer without the formation of an emulsion (Velikovskii and Druzhina, *Neft, Khoz.* 1933, 25, 48; Bisko, *Refiner*, 1937, 16, 72). For similar reasons the extraction of distillates is limited to those of relatively low viscosity, generally not exceeding that of spindle oil (approximately 50 centistokes, at 20°). More viscous oils may of course be washed, if it should prove economical, by heating so as to reduce their viscosity. A rich source of naphthenic acids are the alkaline residues which result from the normal refining treatment of various petroleum distillates, usually subsequent to refining by means of sulphuric acid.

The product obtained by the alkali washing of crude oil, or of its fractions, is in effect an aqueous solution of sodium naphthenate, together with a certain amount of hydrocarbon material dissolved in the soap solution; this is removed by extraction with a light solvent after diluting the solution, and acidification of the separated aqueous layer liberates the naphthenic acids. Other methods of recovery include the salting out of the naphthenic soaps from aqueous solution with brine, or the use of sulphur dioxide for the neutralisation of the alkaline wash liquors.

In the case of crudes, or reduced crudes, distilled over caustic soda, the sodium naphthonate formed is retained in the solid residue, and may be recovered therefrom by treatment with water or alcohol, and the further processing of the resultant solution as already described.

Naphthenic acids recovered in this manner, particularly those obtained from crude, or from reduced crude, and not from distillates, contain,

in addition to the acids themselves, varying quantities of resinous and asphaltic bodies which have to be removed by further treatment. Furthermore there are also present phenols, which after naphthenic acids, form the principal oxygen-containing constituents of petroleum. Phenols are particularly evident in naphthenic acids recovered from the lighter cuts, such as kerosene and gas oil. In those cases where the alkaline residues from the refining of cracked products are processed, they may even form the main by-product. The separation of phenols from naphthenic acids is a matter of some difficulty; normally, in the case of commercial acids—except in the relatively rare cases when these have been extracted from cracked materials—phenols are present in a small proportion of the total bulk and it is not usual to separate them. Separation methods which have been suggested are mainly based on the fact that extraction of a naphthenic acid-phenol mixture with sodium carbonate solution will dissolve the acids only, leaving the phenols to be taken up by subsequent treatment with caustic soda (*cf.* Campbell, *ibid.* 1935, 14, 381). Such a separation is, however, by no means complete, and in cases where a complete separation is required, as in the chemical investigation of naphthenic acid structure, it is necessary to eliminate phenols by laboratory methods, inapplicable on an industrial scale.

*Refining.*—For some industrial purposes, the naphthenic acids are utilisable in the condition in which they are recovered; however, for the majority of applications, it is necessary to subject them to some degree of refining, both in order to decrease their characteristic and disagreeable odour, and also to raise the acid content by the elimination of unsaponifiable matter.

Whilst a slight degree of success is attained by the treatment of naphthenic acids in a manner analogous to that utilised for the refinement of petroleum products, such as treatment with sulphuric acid and adsorbent earths, or by various oxidising agents, it is necessary for satisfactory refining to utilise distillation. Owing to their high boiling points, distillation at atmospheric pressure cannot be accomplished without a considerable degree of decomposition, and either steam distillation or vacuum distillation is required. Final refining of the distillate can be effected either by a treatment with sulphuric acid and earth, or with earth alone (Goldberg and Kochoeva, *Masl. Zhir. Delo*, 1935, 11, 594). Various solvent refining methods have been proposed for naphthenic acids, but do not appear to have achieved commercial success.

*Physical and General Properties.*—The acids obtained in this manner are oily liquids; their colour varies from dark red to almost colourless, depending upon the degree of refinement to which they have been subjected. The specific gravity of naphthenic acids, which in many cases decreases with increasing molecular weight, can lie within the range 0.93–1.09, although the majority of commercial acids are within the narrower limits of 0.94–0.99. The product of specific gravity and refractive index has been proposed by Schutze *et al.* (*Ind. Eng. Chem.*

[*Anal.*] 1940, 12, 262) as a guide to the classification of naphthenic acids. The boiling-points of the acids, at atmospheric pressure, are from about 215° upwards, although only the lower members can be distilled at atmospheric pressure without decomposition. The melting-points of the majority of acids are very low, in some cases below –80°, although solid acids, of a tertiary structure, have been isolated (Kennedy, *Nature*, 1939, 144, 832; *cf.* Shive *et al.*, *J. Amer. Chem. Soc.* 1940, 62, 2744; 1941, 63, 2979).

Naphthenic acids have a pronounced and characteristic odour, which varies with their origin and degree of refining; the odour is more marked in the lower members of the series. The acids are completely miscible with hydrocarbons; the lower members have a slight solubility in water; they are soluble in sulphuric acid by which they are attacked but slightly. The acid values decrease with increasing molecular weight, the viscosities increase, and are of the same order, although higher, than of the petroleum fractions from which the acids are derived.

Many grades of acids are commercially available. Until fairly recently, the only acids on the market were those obtained from Russian and Roumanian crudes, being produced as a by-product of the refining of the kerosene- and spindle-oil cuts. For some years, however, acids from American crudes have taken an increasingly large share of the market, and these acids, in addition to being obtained from the lighter petroleum fractions, are also recovered from the heavier lubricating oil cuts, as well as from the original crudes or topped crudes. This change in the origin of naphthenic acids has meant that the importance previously attached to the acid value as a criterion of quality is now less, since, of course, with increasing molecular weight, the acid value will fall. Hence it is of more importance to know the content of the acids in unsaponifiable matter, since this factor represents the amount of inert non-reacting material, as far as the majority of the uses of naphthenic acids are concerned. It is now generally recognised that a high quality naphthenic acid should have a content of unsaponifiable matter of below 10%. Acid values for commercial grades of naphthenic acids range from about 150–170 for acids derived from crudes and from lubricating oils, equivalent to a molecular weight of about 300, to about 250 or higher for acids from the lower boiling fractions of petroleum. Optical activity has been observed in naphthenic acids, but there is considerable evidence that this is due to impurities and not to the acids themselves.

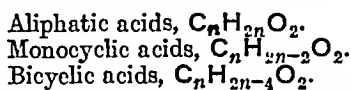
The acids are soluble in liquid sulphur dioxide and, in the refining of oils by the Edeleanu process, they tend to be concentrated in the extract phase.

#### Chemical Constitution.

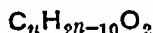
For the purpose of the investigation of the structure of naphthenic acids, it is necessary to obtain them in a considerably purer condition than are the acids of commerce. This may be accomplished by careful vacuum distillation and further purification by chemical methods. These

latter may consist in the conversion of the acids to their methyl esters, which boil on the average at a temperature  $50^\circ$  lower than the acids themselves, followed by redistillation of these esters and saponification for the recovery of the acids. Other methods include the preparation of the amides and oxalates of the acids, and also the resaponification of the commercial acids, followed by extraction of hydrocarbons by light solvents, sometimes under pressure, and liberation of the acids, with subsequent molecular distillation.

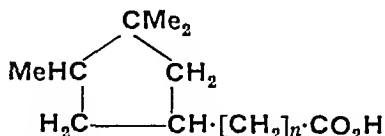
Much of our knowledge of the structure of naphthenic acids is due to the work of von Braun ("The Science of Petroleum," London, 1938, Vol. 2, p. 1007; *Re. Cong. Mond. Petr.* 1937, 2, 127). As a result of his investigations, and those of others, it may be said that, broadly speaking, the acids up to about  $C_7$  are aliphatic in character, those from  $C_8$  to about  $C_{12}$  monocyclic, and acids up to about  $C_{23}$  bicyclic. The composition of the acids is represented by the following type formulæ:



More highly condensed systems, up to



have also been detected (Harkness and Bruun, *Ind. Eng. Chem.* 1940, 32, 499). Goheen (*ibid.*, p. 503) has also found evidence of the presence of more than two rings per molecule, and has prepared naphthene hydrocarbons from naphthenic acids. In the majority of naphthenic acids so far examined, the ring structure is predominantly a cyclopentane ring with the carboxyl group at the end of an alkyl side-chain. The formula below represents a typical structure of medium molecular weight naphthenic acids, such as have been found in nearly all crudes, where  $n$  can be up to 5 or over.



It is of interest to compare this structure with that of the naturally occurring chaulmoogric and hydnocarpic acids, which are also based on five-membered rings. The presence of acids with a six-membered ring is suggested by parachor measurements on methyl esters of naphthenic acids from Russian crudes (Lapkin, *J. Gen. Chem. Russ.* 1939, 9, 1332).

Acids containing a cyclohexano structure have been isolated from Californian petroleum (Ney *et al.*, *J. Amer. Chem. Soc.* 1943, 65, 770). The stability of naphthenic acids to reagents, and the absence of halogen absorption, indicate that unsaturation is absent.

The acidic constituents from cracked distillates, in addition to being rich in phenols, as already mentioned, also contain straight chain acids in considerably greater quantity than is found in acids from crude oil or its fractions.

**Chemical Properties.**—The naphthenic acids show the properties that would be expected of

them as monocarboxylic organic acids. They behave in a very similar manner to the fatty acids and, like them, form a series of metallic salts (soaps). Similarly to the fatty-acid soaps, the alkali soaps of the naphthenic acids are soluble in water and almost insoluble in hydrocarbons, whilst the soaps of other metals (except silver) are water-insoluble and oil-soluble.

Naphthenic acids have a markedly acidic character, being more acidic than the higher fatty acids, and will displace weaker acids from their salts, even showing this tendency to a slight extent, at elevated temperature, in the case of the salts of strong acids such as chlorides.

Many metals are attacked by naphthenic acids, and among the commoner metals the degree of attack is greatest in the case of lead and least (almost nil) in that of aluminium, with zinc, copper, and iron occupying intermediate positions in that order.

The naphthenic acids, like the fatty acids, form amides, esters (including glycerides) and other derivatives. On reduction they yield the corresponding alcohols.

### Uses.

The utilisation of naphthenic acids may be divided into that of the acids as such, and that of the acids in the form of their naphthenates, of which sodium naphthenate is the most frequently used. In certain cases a mixture of naphthenic acids and sodium naphthenate is supplied, since, unlike sodium naphthenate, such a mixture is liquid and pumpable, and, on receipt, it may be converted either entirely into the soap or into the free acid by the addition of the appropriate quantity of alkali or mineral acid (Shipp, *Oil and Gas J.* 1936, 34, No. 44, p. 56). Concentrated aqueous solutions of sodium naphthenate (up to 50%) are likewise fluid.

One of the earliest uses of naphthenic acids was as an aid in petroleum refining for the prevention of emulsion formation. Naphthenic acids have also been used as a solvent for rubber, in rubber reclamation, and for admixture with tung oil to retard the gelatinisation of the latter. They also enter into the composition of various soluble oils (cutting oils) and greases. They have also been used as a diluent in refining operations for the identification of oil streams. Uses as wetting agents, and in ore flotation, as well as for mosquito control, have also been suggested.

In the form of soaps, the sodium salt of naphthenic acid is that most frequently employed, either for use as such or as the starting material for the preparation of other soaps. The sodium salt itself has been used for a considerable time as a cheap detergent; it is also employed as an emulsifier in the preparation of bituminous paints, particularly such as have been used in recent years for camouflage purposes. Sodium naphthenate is a constituent of various types of greases; in solution it has some bactericidal activity (a 1% solution has a phenol coefficient of 3) and it has been used as a component of antiseptic soaps.

Ammonium naphthonate in aqueous solution is a good solvent for hydrocarbons and this

property is made use of in the preparation of emulsions. *Calcium* naphthenate has a considerable solubility in fatty oils, and has been used to increase the viscosity of the latter; it can also act as an oxidation catalyst for mineral oils, *e.g.*, in the oxidation of hydrocarbons for the formation of synthetic fatty acids. It may be noted that the calcium soaps of the lower acids have but slight solubility in oils. *Aluminium* naphthenate forms a very consistent mass; it is used as a thickener for mineral oils, as a constituent of greases, and also in the production of extreme pressure lubricants; for the latter purposes, however, *lead* naphthenate is more widely employed. *Aluminium* naphthenate is also used for the waterproofing of fabrics. The naphthenates of *lead*, *cobalt*, and *manganese* have acquired wide use as driers ("Soligen") in paint manufacture (Greenfield, *Paint Manuf.* 1935, 5, 154; Curwen, *ibid.* 1936, 6, 38); they are stated to be considerably superior in this respect to the fatty acid salts of these metals, being more soluble and stable than the oleates and linoleates. It is in the manufacture of driers that a large proportion of the naphthenic acid output finds utilisation. The *cobalt* salt is the basis for a sensitive test for hydrogen peroxide, which, it is stated, is not given by ozone (Charitschkov, *Chem.-Ztg.* 1910, 34, 50, 479). *Copper* naphthenate is used as a wood preservative and for the impregnation of sandbags and other textiles, to prevent rotting (*cf.* Marsh *et al.*, *Ind. Eng. Chem.* 1944, 36, 176). *Zinc* naphthenate is likewise used for the protection of fabrics, whilst *cerium* naphthenate is stated to be a good waterproofing agent. The use of naphthenates for the preservation of cellulose, and of textiles generally, has been discussed by Carter (*Chem. Age*, 1944, 51, 517). *Tin* naphthenate has been suggested as an oxidation inhibitor for mineral oils. Naphthenates of *bismuth* and *lithium* have been employed for medicinal purposes, as have the *ureides*.

The addition of metallic naphthenates (in quantities of from 0.5% upwards) to fuel oils has the effect of markedly diminishing the soot produced. Some metallic naphthenates are employed as wetting agents for the dispersion of pigments in printing-ink manufacture, and various naphthenates, as well as the acids themselves, are used as components of insecticidal and fungicidal sprays. The fungicidal action of naphthenic acids has been examined by Marsh (*l.c.*).

Generally speaking it may be said that the naphthenates form a convenient method of obtaining a metal radical in an oil-soluble form.

The preparation of heavy metal naphthenates may be accomplished by several methods of which the following are the principal:

- (i) By the double decomposition of sodium naphthenate and a salt of the metal, whereby the metallic naphthenate is precipitated.
- (ii) By the interaction of the metallic oxide with naphthenic acid; this may conveniently be carried out in a medium wherein the resultant naphthenate is soluble.

The discoloration of naphthenates, sometimes observed on storage, may be diminished by the use of inhibitors.

Salts of naphthenic acids with organic amines have found application as emulsifying and wetting agents. The use of naphthenic acid derivatives in synthetic resin manufacture has been proposed.

Naphthenic alcohols, prepared by the catalytic hydrogenation of the acids, have been employed as wetting agents, and as detergents, for which purposes esters and other derivatives of naphthenic acids have also found some application.

### Analysis.

The qualitative detection of naphthenic acids by means of the copper salt has already been mentioned.

Like the fatty acids, naphthenic acids may be titrated in alcoholic solution, employing phenolphthalein as indicator.

For the determination of the naphthenic acid content of samples of commercial acid, containing appreciable quantities of unsaponifiable matter, a modification of the Hönig and Spitz (*Z. angew. Chem.* 1891, 4, 565; *J.C.S.* 1893, 64, ii, 102) method is employed. This consists in refluxing about 10 g. of the material for  $\frac{1}{2}$  hour with 50 ml. of *n*-alcoholic KOH; 50 ml. of water are then added, and the mixture extracted three times with 40 ml. each time of light petroleum (b.p. 60–80°). The petroleum solution, containing the unsaponifiable matter, is then evaporated on the water-bath and the residue weighed.

The residual alkaline soap solution is evaporated to remove the alcohol, and acidified to Methyl Orange with sulphuric acid. The liberated naphthenic acids are then extracted with light petroleum, and the extracts washed with saturated sodium sulphate solution until free from mineral acid, and then with a small quantity of distilled water to remove all the sodium sulphate. The solvent is finally removed by evaporation and the acids weighed. A cross-check, indicating the extent of the unavoidable loss of volatile unsaponifiable constituents, is afforded by the ratio of the acid values of the original mixture and of the pure acids.

A similar method, varying slightly from the above, is described by Klotz and Littmann (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 76).

The determination of naphthenic acids in the presence of mineral oil and of petroleum sulphonic acids, is a matter of some importance, and has been the subject of work by Pilat and Sereda (*Fettchem. Umschau*, 1934, 41, 171). The basis of their method is the removal of hydrocarbons by ethyl ether, and the subsequent differentiation between naphthenic and sulphonic acids by the fact that the sulphonic acids, being the stronger, react with sodium chloride, whilst the naphthenic acids do not. The determination of naphthenic acids in heavy petroleum residues has been described by Schaefer (*Fette u. Seifen*, 1937, 44, 146),

### SULPHO-NAPHTHENIC ACIDS.

The term "sulpho-naphthenic acids" is one which is frequently misused. It denotes naph-



thenic acids which, by the action of sulphuric acid or of oleum, have had a sulphonic group introduced into the molecule. In practice the term is often misapplied to refer to other sulphonic acids, i.e., acids obtained as a by-product during the refining of petroleum fractions by sulphuric acid or oleum by the sulphonation of the more easily attackable hydrocarbons, and which are substances quite distinct from naphthenic acids.

Genuine sulpho-naphthenic acids can be produced by the treatment of naphthenic acids with oleum, despite the fact that naphthenic acids are fairly resistant to such treatment. Investigations by Kisielowicz *et al.* (Re. Cong. Mond. Petr. 1937, 2, 435) showed that on the mixing of naphthenic acids with 100% (by volume) of oleum (10% free  $\text{SO}_3$ ) not more than 50% of the naphthenic acids were sulphonated, and at that, only in the case of acids of higher molecular weight, which were the more easily attacked. It thus appears that sulpho-naphthenic acids will occur in refining operations only as a result of the treatment of highly acidic petroleum distillates with oleum, when they will be admixed with other sulphonic acids, and it is therefore extremely unlikely that the majority of the commercial products which have been described as sulpho-naphthenic acids are in fact truly sulphonated naphthenic acids. Unless these latter are meant it would be preferable to employ the term "petroleum sulphonic acids" (to distinguish them from sulphonated fatty acids) in respect of petroleum refining by-products, and to restrict the term "sulpho-naphthenic acids" to genuine sulphonated naphthenic acids. The term "naphthene-sulphonic acids," which is also sometimes met with for petroleum sulphonic acids, whilst admittedly less open to objection than "sulpho-naphthenic acids" is not free from ambiguity, and also has the disadvantage that it tends to pre-suppose a naphthene structure for these compounds, which is not necessarily always the case.

Sulphonated naphthenic acids have been produced for various purposes, amongst which may be mentioned use as wetting agents and as substitutes for Turkey-red oil.

**Literature.**—In addition to the references quoted, the following should be consulted for a more detailed discussion of the subject:

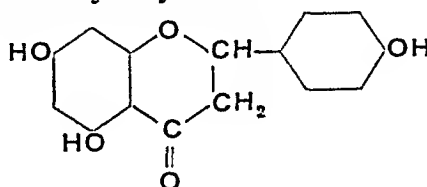
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- M. Naphtali, "Chemie, Technologie und Analyse der Naphthensäuren," Stuttgart, 1927, and the supplementary volume "Naphthensäuren und Naphthensulfosäuren," Stuttgart, 1934.
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V. B.

NAPHTHITE (v. Vol. IV, 475a).  
 NAPOLEONITE (v. Vol. IV, 8b).  
 NARCEINE (v. OPIUM).  
 NARCISSINE (v. Vol. VII, 428c).  
 NARCOTINE (v. OPIUM).  
 NARCOTOLINE (v. OPIUM).  
 NARCYLEN (v. Vol. I, 79b; 367d).

**NARINGIN** is a glycoside obtained from the flowers and fruit of *Citrus decumana* Murr. (grapefruit) (Will, Ber. 1885, 18, 1311; 1887, 20, 294, 1186). It is the bitter principle of grapefruit, is sparingly soluble in water and is strongly laevorotatory,  $[\alpha]_D^{19} -82.1^\circ$  in alcohol.

Naringin,  $\text{C}_{27}\text{H}_{32}\text{O}_{14} \cdot 2\text{H}_2\text{O}$ , m.p.  $171^\circ$ , is hydrolysed by boiling dilute sulphuric acid and yields *d*-glucose, *l*-rhamnose, and naringenin, or 5:7:4'-trihydroxyflavanone:



(Zoller, Ind. Eng. Chem. 1918, 10, 371; Asahina and Inubuse, Ber. 1928, 61 [B], 1514; J. Pharm. Soc. Japan, 1929, 49, 128). Naringin is not hydrolysed by emulsin, but by the action of an enzyme, apparently an  $\alpha$ -glucosidase, present in celery seed, it yields naringenin and a disaccharide (Hall, Chem. and Ind. 1938, 473). The glucorhamnose residue is attached to position 7 of the aglucone naringenin (Asahina and Inubuse, *loc.*; Rangaswami, Seshadri, and Veeraraghaviah, Proc. Indian Acad. Sci. 1939, 9, A, 328).

The synthesis of naringenin was effected by condensing phloroglucinol with the chloride of *p*-carbethoxycinnamic acid (Rosenmund and Rosenmund, Ber. 1928, 61 [B], 2608; Shinoda and Sato, J. Pharm. Soc. Japan, 1928, 48, No. 560, 117). Naringenin is reduced by hydrogen in the presence of palladium to phloretin ( $\beta$ -*p*-hydroxyphenylpropionylphloroglucinol) (Franck, Chem. Zentr. 1914, II, 253; Rosenmund and Rosenmund, *loc.*).

From the bark of the peach, Shinoda and Uyeda (J. Pharm. Soc. Japan, 1929, 49, 97) isolated a compound apparently identical with naringenin.

E. J. C.

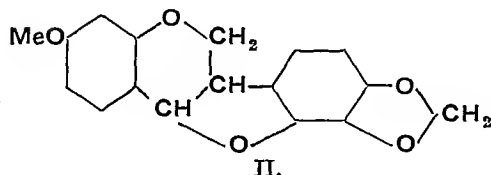
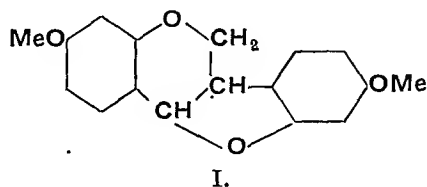
**NARRAWOOD** (*Pterocarpus* spp.), a well-known Philippine wood, is classified with Sanderswood (*Pterocarpus santalinus* Linn.), Barwood (*Baphia nitida* Lodd) and Camwood (variety of *Baphia nitida*) under the name "insoluble red" woods, so called on account of the sparing solubility in water of the resinous colouring matters which they contain and to distinguish them from the "soluble red" woods of the type of logwood.

By extracting narrawood with alcohol, the colouring matter, *narrin*, is obtained as a dark red amorphous powder decomposing at  $180^\circ$ , readily soluble in alcohol, insoluble in chloroform (Brooks, Philippine J. Sci. 1910, 5, A, 448). *Narrin* forms a copper salt of composition  $(\text{C}_{15}\text{H}_{13}\text{O}_6)_2\text{Cu}$  and on fusion with alkali gives phloroglucinol and resorcinol. By slow oxidation with permanganate vanillin is produced, and when distilled with zinc dust *narrin* yields a small amount of resorcinol dimethyl ether. According to Brooks, *narrin* is not identical with the santalin of sanderwood.

The dyeing properties of *narrin* are similar to those of santalin, but the shades produced are not very fast to soap.



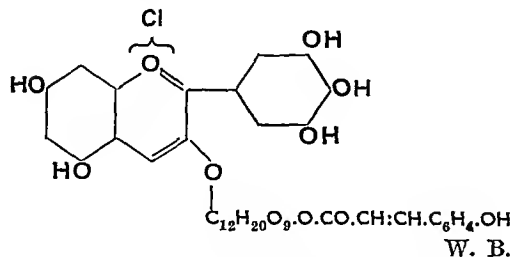
The "insoluble red" woods invariably contain the colourless constituents *pteroecarpin*,  $C_{16}H_{11}O_4(OMe)$ , m.p.  $164.5^\circ$ , and *homopteroecarpin*,  $C_{15}H_{10}O_2(OMe)_2$ , m.p.  $87^\circ$ , of which the latter is the more abundant. Homopteroecarpin, which is devoid of hydroxyl or carboxyl groups, is converted by catalytic reduction into *l*-dihydrohomopteroecarpin containing a phenolic group, and this on oxidation gives rise to 7-methoxychroman-3-carboxylic acid. Homopteroecarpin is considered to be 4:2'-oxido-7:4'-dimethoxyisoflavan (I) and *l*-dihydrohomopteroecarpin 2'-hydroxy-7:4'-dimethoxyisoflavan. To pteroecarpin, formula (II) is ascribed



(Dieterle and Leonhardt, Arch. Pharm. 1929, 267, 81; Leonhardt *et al.*, *ibid.* 1935, 273, 53, 447; Raudnitz and Perlmann, Ber. 1935, 68 [B], 1862; McGookin, Robertson, and Whalley, J.C.S. 1940, 787; Späth and Schläger, Ber. 1940, 73 [B], 1).

E. J. C.

**NASUNIN**, the colouring matter of the eggplant (*Solanum melogena* L. var. *erulentum* Ness), is considered to be a *p*-hydroxycinnamoyl derivative of a delphinidin-3-bioside, the acyl group being attached to the biose residue. It is thus closely related structurally to *violantin* (Kuroda and Wada, Bull. Chem. Soc. Japan, 1936, 11, 272),



W. B.

**NATROJAROSITE** (*v.* Vol. VII, 81a).

**NATROLITE**. One of the commonest members of the zeolite family of hydrous silicate minerals. Its composition is



and it crystallises in the monoclinic system, though with very close approximation to orthorhombic symmetry. Crystals are sometimes slender prismatic and almost square in cross-section, but are usually acicular to fibrous, whence the colloquial name "needle zeolite."

The mineral has perfect prismatic cleavage, a hardness of about 5, and  $\rho$  2.25. It is generally colourless or white, but may be tinted yellow to red, and has a vitreous lustre. Like the "artificial zeolites" used in water-softening, natrolite has high base-exchange capacity and electrical conductivity. The natural mineral is typically found as radiating acicular groups in the steam-cavities of basalts.

Reference.—M. H. Hey, Min. Mag. 1932, 23, 243.

D. W.

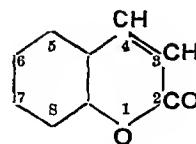
**NATRON**. A mineralogical term (from the ancient *νίτρον*, soda) for the hydrated sodium carbonate,  $Na_2CO_3 \cdot 10H_2O$ , crystallising in the monoclinic system. Since this hydrate crystallises only at temperatures below  $20^\circ$ , it is only under exceptional conditions that it is likely to be found in the natron or soda lakes of desert regions; and if formed it would soon effloresce into the monohydrate,  $Na_2CO_3 \cdot H_2O$ , known as *thermonatrite*. According to Dana it exists only in solution. The native soda met with in the regions of natron lakes consists for the most part of the salt  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$  known as *trona*, together with *thenardite* ( $Na_2SO_4$ ) and *halite* (NaCl).

L. J. S.

**NATURAL COUMARINS**. The natural coumarins are lactones derived from the naturally occurring parent substance coumarin (I) (*v.* Vol. III, p. 412a) which has been found in 75 different botanical species. Many of its simple derivatives are present in plants as glucosides whilst others, together with the more complex coumarins, have only been extracted in the free state, although it has been suggested that many of them may also be combined with glucose. Hitherto no coumarin glucosides have been detected.

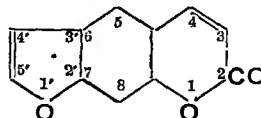
The natural coumarins fall into three main classes:

I. The simple coumarins derived from coumarin:

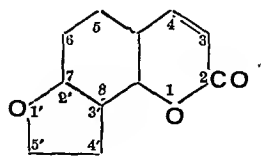


II. The furanocoumarins.

(a) Derivatives of psoralene, 2':3':7:6-furanocoumarin:

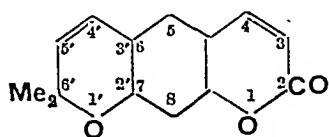


(b) Derivatives of angelicin, 2':3':7:8-furanocoumarin:

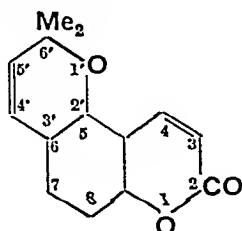


III. The pyrenocoumarins or chromeno- $\alpha$ -pyrones:

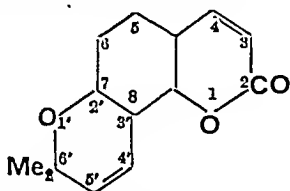
(a) Derivatives of xanthyletin, 6':6'-dimethyl-2':3':7:6-pyrenocoumarin:



(b) Derivatives of 6':6'-dimethyl-2':3':5:6-pyrenocoumarin:



(c) Derivatives of seselin, 6':6'-dimethyl-2':3':7:8-pyrenocoumarin:



(see Späth, Ber. 1937, 70 [A], 83. In addition to reviewing the field, with references, this paper gives many botanical sources of the natural coumarins). A few additional plant species have been included here and the official names have been checked with Index Kewensis.

In those cases where the official name of a botanical species differs from that which has been used to designate the natural coumarin the synonym of the plant has been included in brackets after the Index Kewensis title.

## I. THE SIMPLE COUMARINS.

### Degradation.

The glucosides are hydrolysed by dilute mineral acids to yield glucoside and the aglucones.

The coumarins, on catalytic hydrogenation, furnish 3:4-dihydrocoumarins which are oxidisable to succinic acid by the disruption of the  $\alpha$ -pyrone ring. Methylation of coumarins by means of dimethyl sulphate and alkali also opens the lactone ring with the production of *o*-methoxycinnamic acids which, on oxidation, are converted into *o*-methoxybenzoic acids. The hydroxy-coumarins must first be methylated with diazomethane before carrying out this reaction.

Alkali fusion of coumarins gives rise to phenols.

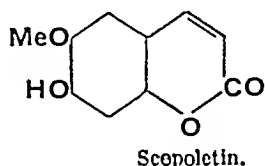
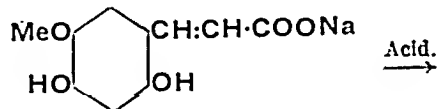
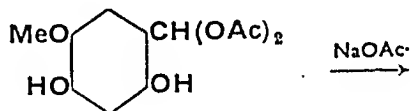
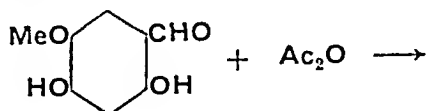
Unsaturated side chains are detected by oxidation of the hydrogenated coumarins, when fatty acids are obtained. An alternative method is the isolation of aldehydes or ketones by ozonisation.

Fission of the coumarin ethers is brought about by means of acetic acid containing a trace of sulphuric acid, when an alcohol and a phenol are the products.

### Synthesis.

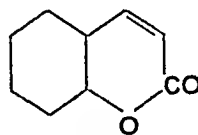
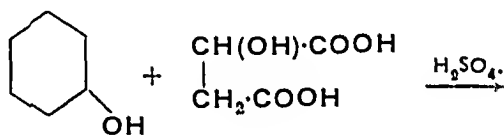
*Glucosides.*—The glucosides have been synthesised by the action of *O*-tetra-acetylglucosidyl bromide on the phenols in the presence of silver oxide and quinoline.

*Coumarins.*—1. Perkin's method:



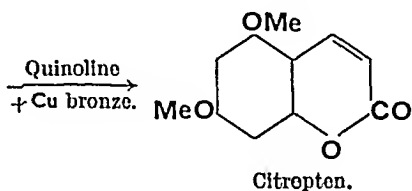
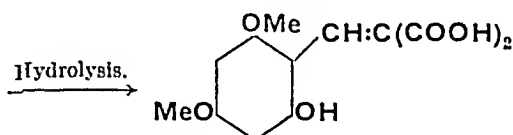
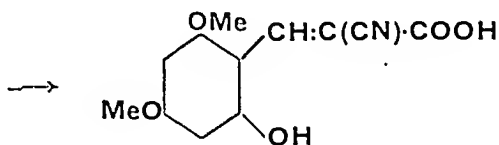
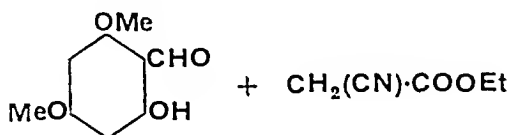
Scopoletin.

2. Von Pechmann's method:



Coumarin.

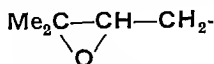
3. Ester method:



Citropten.

Acetoacetic ester or malonic ester may also be used (see Chakravarti, Proc. Nat. Acad. Sci. India, 1939, 5, 235; Shah, *ibid.*, p. 243. These two papers give a general account of the synthetical methods employed in coumarin formation, and the first contains a bibliography).

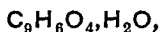
Aculeatin,  $C_{16}H_{15}O_5$ , 5:7-dimethoxy-6-



coumarin (the positions of substituents in the benzene ring are not stated, but cf. *Toddolactone*). Found in *Toddalia aculeata* Pers., m.p. 113°,  $[\alpha]_D^{24} +16.8^\circ$  in EtOH (see Dutta, J. Indian Chem. Soc. 1942, 19, 425).

Aculeatin Hydrate v. *Toddolactone*.

*Æsculetin*, *cichorigenin*, *esculetin*, 6:7-dihydroxycoumarin, occurs as the 6-glucoside, *æsculin*,  $C_{15}H_{16}O_9 \cdot \frac{1}{2}H_2O$ , m.p. 205° decomp.;  $[\alpha]_D^{11} -146^\circ$  in MeOH; *methyl ether*, m.p. 225°; *penta-acetyl deriv.*, m.p. 130°. It is also found as the 7-glucoside,  $C_{16}H_{16}O_9 \cdot 2H_2O$ , *cichoriin*, in *Cichorium intybus* Linn., m.p. 216°; *methyl ether*, m.p. 218°; *penta-acetyl deriv.*, m.p. 217-218°. Both glucosides yield the same aglucone, *æsculetin*, on acid hydrolysis and this substance also occurs in *Asculus pavia* Linn. and various *Fraxinus* species. *Æsculetin*,

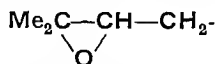


m.p. 276°, soluble in hot water with blue fluorescence; 6-*methyl ether* v. *Scopoletin*; 7-*methyl ether*, m.p. 185° (*acetyl deriv.*, m.p. 164-166°). *Dimethyl ether*, m.p. 146°; *diacetyl deriv.*, m.p. 133-134° (see Head and Robertson, J.C.S. 1939, 1266; 1930, 2434; Macbeth, *ibid.* 1931, 1288; Seka and Kallir, Ber. 1931, 64 [B], 622; Merz, Arch. Pharm. 1932, 270, 476).

*Æsculin* v. *Æsculetin*.

*Ammoresinol*,  $C_{24}H_{30}O_4$ , 4:7-dihydroxy-3- $\text{Me}_2\text{C}:\text{CH}[(\text{CH}_2)_2 \cdot \text{C}(\text{Me})\text{CH}_2] \cdot \text{CH}_2$ -coumarin, m.p. 109°; *diacetyl deriv.*, m.p. 102-103°; *dibenzoyl deriv.*, m.p. 75° (see Raudnitz et al., Ber. 1936, 69 [B], 1956; Späth and Zajic, *ibid.*, p. 2448).

Aurapten,  $C_{15}H_{16}O_4$ , 7-methoxy-8-



coumarin, a fish poison extracted from orange peel, m.p. 98°,  $[\alpha]_D^{20} -33.4^\circ$  in EtOH. Boiling 20%  $H_2SO_4$  gives *isaurapten*, m.p. 66° (see Bohme and Schneider, *ibid.* 1939, 72 [B], 780).

Ayapanin v. *Herniarin*.

Ayapin,  $C_{10}H_6O_4$ , 6:7-methylenedioxy-coumarin, m.p. 231-232° in vac. (see Späth et al., *ibid.* 1937, 70 [B], 702; Bose and Ghosh, Current Sci. 1936, 5, 295).

Chrysotropic Acid v. *Scopoletin*.

Cichorigenin v. *Æsculetin*.

Cichoriin v. *Æsculetin*.

Citropten,  $C_{11}H_{10}O_4$ , *limettin*, 5:7-dimethoxycoumarin. Occurs in essential oil of limes, other Citrus species and *Zanthoxylum setosum* Hemsl., m.p. 147.5°, soluble EtOH,  $C_6H_6$ , with violet fluorescence (see Heyes and Robertson, J.C.S. 1936, 1831; Nakazawa, J. Pharm. Soc. Japan, 1935, 55, 788).

Daphnetin, 7:8-dihydroxycoumarin. Occurs as the 7-glucoside, *daphnin*,  $C_{15}H_{16}O_9 \cdot 2H_2O$ , m.p. 228-229°,  $[\alpha]_D^{22} -114.66^\circ$  in MeOH. The aqueous solution has a bitter taste. It is also present in *Arthrosolen polycephalus* C. H. Mey, as a glucoside,  $C_{15}H_{15}O_9$  (position of glucose residue not determined), m.p. 197-198°. Both glucosides, on acid hydrolysis, yield daphnetin,  $C_9H_6O_4$ , pale yellow needles, m.p. 256°; *dimethyl ether*, m.p. 119-121°; *diacetyl deriv.*, m.p. 137° (see Hattore, *ibid.* 1930, 50, 539; Gardini, Gazzetta, 1940, 70, 611).

Daphnetin Glucoside v. *Daphnetin*.

Daphnin v. *Daphnetin*.

Esculetin v. *Æsculetin*.

Fabiatriin v. *Scopoletin*.

Fraxetin, 7:8-dihydroxy-6-methoxycoumarin. Present in the ash and in *Asculus turbinata* Blume, as the 8-glucoside, *fraxin*,  $C_{16}H_{18}O_{10} \cdot 3H_2O$ , yellow needles, m.p. 205°. Alkaline solution has a blue-green fluorescence. Acid hydrolysis yields fraxetin,  $C_{10}H_8O_5$ , yellow plates, m.p. 237°; 7-*methyl ether* v. *Fraxidin*; 8-*methyl ether* v. *isofraxidin*; *dimethyl ether*, m.p. 103-104° (see Simada, J. Pharm. Soc. Japan, 1937, 57, 618; Späth and Dobrowolny, Ber. 1938, 71 [B], 1825; Wessely and Demmer, *ibid.* 1929, 62 [B], 120).

Fraxidin,  $C_{11}H_{10}O_5$ , *fraxetin*, 7-*methyl ether*, 8-hydroxy-6:7-dimethoxycoumarin, m.p. 196-197° (see Späth and Sienkiewiczowa *ibid.* 1937, 70 [B], 1672).

Fraxin v. *Fraxetin*.

Fraxinol,  $C_{11}H_{10}O_5$ , 6-hydroxy-5:7-dimethoxycoumarin, m.p. 172-173°; *methyl ether*, m.p. 76-77°; *acetyl deriv.*, m.p. 140-141° (see Späth and Sienkiewiczowa, *ibid.* 1937, 70 [B], 698).

Gelseminic Acid v. *Scopoletin*.

Herniarin,  $C_{10}H_8O_3$ , *ayapanin*, 7-methoxycoumarin, *umbelliferone methyl ether*. Occurs in the leaves of *Herniaria hirsuta* Linn. and in *Eupatorium triplinerve* Vahl. (*E. ayapanum* Vent.), m.p. 118-119°, soluble in conc.  $H_2SO_4$  with blue fluorescence; *oxime*, m.p. 138°; *phenylhydrazone*, m.p. 115° (see Bose and Roy, J. Indian Chem. Soc. 1936, 13, 580; Dey et al., *ibid.* 1935, 12, 140).

Hydrocoumarin,  $C_9H_8O_2$ , *melilotic lactone*, *melilotin*, *melilotol*, 3:4-dihydrocoumarin. Present in *Melilotus officinalis* Lam., m.p. 25°, b.p. 272° (see Palfray, J. Amer. Chem. Soc. 1941, 63, 3541).

*isoFraxidin*,  $C_{11}H_{10}O_5$ , *fraxetin*, 8-*methyl ether*, 7-hydroxy-6:8-dimethoxycoumarin, m.p. 148-149° (see Späth and Dobrowolny, Ber. 1938, 71 [B], 1831).

Limettin v. *Citropten*.

Melilotic Lactone v. *Hydrocoumarin*.

Melilotin v. *Hydrocoumarin*.

Melilotol v. *Hydrocoumarin*.

Osthenol,  $C_{14}H_{14}O_3$ , 7-hydroxy-8- $\gamma$ -dimethylallylcoumarin, m.p. 124-125°. Shows a green-blue fluorescence in alkali. For *methyl ether* v. *Osthol* (see Späth and Bruck, *ibid.* 1937, 70 [B], 1023).

Osthol,  $C_{15}H_{16}O_3$ , *osthenol methyl ether*, 7-methoxy-8- $\gamma$ -dimethylallylcoumarin. Occurs in *Peucedanum ostruthium* Koch., m.p. 85°, b.p. 145-150° (see Haller and Acree, J. Amer. Chem.

Soc. 1934, 56, 1389; Späth and Bruck, Ber. 1937, 70 [B], 1023; Butenandt and Marten, Annalen, 1932, 495, 187).

Ostruthin,  $C_{19}H_{22}O_3$ , 7-hydroxy-6-methyl- $C:CH[CH_2]_2CMe:CH\cdot CH_2$ -coumarin, m.p. 119°; methyl ether, m.p. 55°; acetyl deriv., m.p. 80° (see Späth and Klager, Ber. 1934, 67[B], 859).

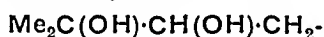
Scopoletin, *chrysotropic acid*, *gelseminic acid*, *æsculetin* 6-methyl ether, 7-hydroxy-6-methoxycoumarin. Occurs in *Scopolia carniolica* Jacq. and in *Murraya exotica* Linn. as the glucoside, *scopolin*,  $C_{16}H_{18}O_9$ , m.p. 218°; soluble in  $H_2SO_4$  with blue fluorescence. A second scopoletin glucoside, *fabiatriin*, has been extracted from *Fabiana imbricata* Ruiz. and Pav.,  $C_{16}H_{18}O_9 \cdot 2H_2O$ , m.p. 226–227°. Evidence as to the identity, or otherwise, of scopolin and fabiatriin is lacking except that, on acid hydrolysis, both compounds yield glucoside and scopoletin,  $C_{10}H_8O_4$ , which is also found free in *Prunus serotina* Ehrh., it has m.p. 205°, is soluble in hot EtOH with blue fluorescence; methyl ether, m.p. 145°; acetyl deriv., m.p. 177° (see Glaser, Arch. Pharm. 1928, 260, 573; Seka and Hallir, Ber. 1931, 64[B], 909; Head and Robertson, J.C.S. 1931, 1241).

Scopolin v. Scopolctin.

Skimmetin v. Umbelliferone.

Skimmin v. Umbelliferone.

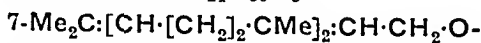
Toddalolactone,  $C_{16}H_{20}O_6$ , *aculeatin hydrate*, 5:7-dimethoxy-6-



coumarin, m.p. 132° (150°),  $[\alpha]_D^{20} +50.9^\circ$  in  $CHCl_3$ . Obtained from aculeatin by digestion with dil.  $H_2SO_4$  at 100°; diacetyl deriv., m.p. 127° (see Späth, Dey, and Tyray, Ber. 1939, 72 [B], 53; Dutta, J. Indian Chem. Soc. 1942 19, 425).

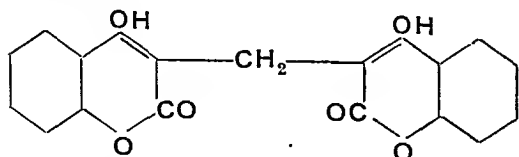
Umbelliferone, *skimmetin*, 7-hydroxycoumarin, present in *Skimmia japonica* Thunb. as a glucoside *skimmin*,  $C_{15}H_{16}O_8 \cdot H_2O$ , m.p. 219–221°, soluble in EtOH with green fluorescence; tetra-acetyl deriv., m.p. 183–184° in vac.; acid hydrolysis yields umbelliferone,  $C_9H_6O_3$ , m.p. 223–224° (with sublimation), soluble in conc.  $H_2SO_4$  with blue fluorescence; methyl ether v. *Herniarin*; acetyl deriv., m.p. 140° (see Böhme, Ber. 1939, 72 [B], 2130; Späth and Neufold, Rec. trav. chim. 1938, 57, 535).

Umbelliprenin,  $C_{24}H_{30}O_3$ ,



coumarin, m.p. 61–63°, occurs in *Angelica archangelica* Linn. (see Späth and Vierhapper, Ber. 1938, 71 [B], 1667).

Methylene-bis-4-hydroxy-3-coumarinyl,  $C_{18}H_{12}O_6$ ,



a hæmorrhagic agent, occurs in spoiled sweet-clove hay. It has m.p. 288–289°, gives a red colour with  $FeCl_3$  in cyclohexanone; dimethyl

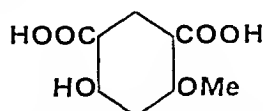
ether, m.p. 168–170°; diacetyl deriv., m.p. 250–252° decomp. (see Stahmann, Huchner, and Link, J. Biol. Chem. 1941, 136, 513).

## II. FURANOCOUMARINS.

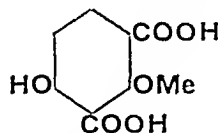
The furanocoumarins are fish poisons and insecticides and are chiefly to be found in plants of the botanical families Rutaceæ and Umbelliferae.

### Degradation.

Oxidation of both types of furanocoumarins yields furan-2:3-dicarboxylic acid. Compounds of type II (a) (see p. 444d) after methylation also give, on oxidation, 4-hydroxy-6-methoxyisophthalic acid:



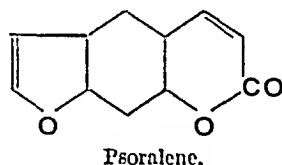
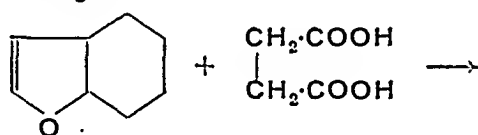
whilst angular compounds of type II (b) on oxidation yield 4-hydroxy-2-methoxyisophthalic acid:



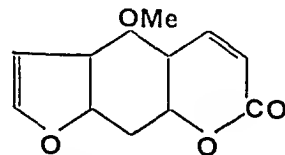
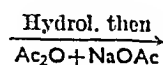
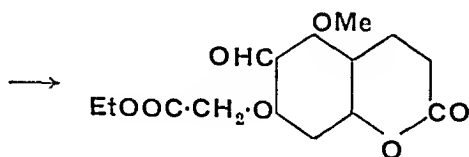
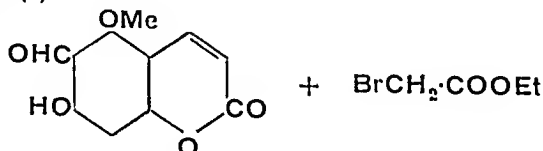
### Synthesis.

The synthesis of the furanocoumarins has been achieved:

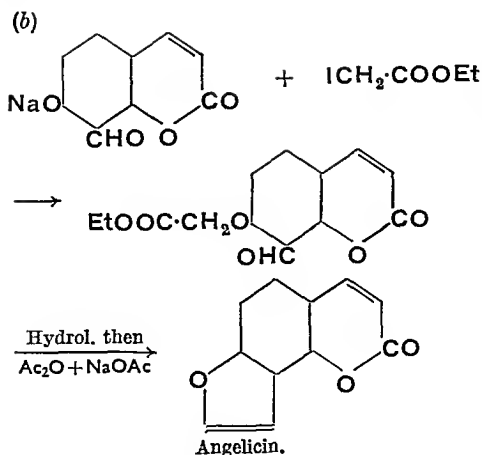
1. From coumarones by completing the  $\alpha$ -pyrone ring:



2. From coumarins by completing the furan ring:  
(a)



Bergapten.



## II (a) Derivatives of Psoralene.

Bergamottin, C<sub>21</sub>H<sub>22</sub>O<sub>4</sub>, *bergaptin*, *bergaptol geranyl ether*,

5-Me<sub>2</sub>C:CH·[CH<sub>2</sub>]<sub>2</sub>·CMe:CH·CH<sub>2</sub>·O-psoralene, m.p. 59–61°. Present in essential oil of bergamot. Heated in high vacuum yields bergaptol (see Späth and Kainrath, Ber. 1937, 70 [B], 2272).

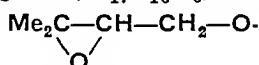
Bergapten, C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>, *heraclin*, *bergaptol methyl ether*, 5-methoxy-psoralene. Occurs in essential oil of bergamot, in *Ruta graveolens* Linn. and in *Seseli indicum* Wight and Arn., m.p. 191° (see Howell and Robertson, J.C.S. 1937, 293; Späth et al., Ber. 1937, 70 [B], 478).

Bergaptin v. Bergamottin.

Bergaptol, C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>, 5-hydroxy-psoralene. Occurs in essential oil of bergamot, m.p. 282°. *Methyl ether v. bergapten*. *Geranyl ether v. bergamottin* (see Späth and Kainrath, *ibid.* 1937, 70 [B], 2272).

Byakangelicin, C<sub>17</sub>H<sub>18</sub>O<sub>7</sub>·H<sub>2</sub>O, 5-(or 8)-methoxy-8(or 5)-Me<sub>2</sub>C(OH)CH(OH)·CH<sub>2</sub>·O-psoralene.—Extracted from the root of *Angelica glabra* Makino. Used as the drug "byakusi." Pale yellow crystals, m.p. 125–126°, [α]<sub>D</sub><sup>25</sup> +24.62° in pyridine. *Diacetyl deriv.*, m.p. 118–119° (see Noguchi, Fujita, and Kawanami, *ibid.* 1938, 71 [B], 344).

Byakangelicol, C<sub>17</sub>H<sub>16</sub>O<sub>6</sub>, 5-methoxy-8-



psoralene. Occurs in the root of *Angelica glabra* Makino, m.p. 106°, [α]<sub>D</sub> +34.77° in pyridine (see Noguchi, Fujita, and Kawanami, *ibid.* 1938, 71 [B], 344; Noguti and Kawanami, J. Pharm. Soc. Japan, 1939, 59, 755).

Fiscusin v. Psoralene.

Heracilin v. Bergapten.

Imperatorin, C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>, *marmelosin*, *xanthotoxol-γγ-dimethylallyl ether*, 8-γγ-dimethylallyloxy-psoralene. Occurs in the fruit of *Aegle marmelos* Correa and in *Angelica glabra* Makino, m.p. 102–103° (see Späth et al., Ber. 1937, 70 [B], 1021).

isoImperatorin, C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>, *bergaptol γγ-dimethylallyl ether*, 5-γγ-dimethylallyloxy-psoralene, m.p. 109° (see Späth and Dobrovolny, *ibid.* 1939, 71 [B], 52).

isoPimpinellin, C<sub>13</sub>H<sub>10</sub>O<sub>5</sub>, 5:8-dimethoxy-psoralene. Occurs in *Seseli indicum* Wight and Arn., m.p. 151° (see Späth and Vierhapper, Monatsch. 1938, 72, 179; Noguchi, Fujita, and Kawanami, Ber. 1938, 71 [B], 344).

Marmelosin v. Imperatorin.

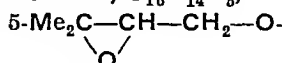
Nodakenetin, C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>, 4':5'-dihydro-5'-Me<sub>2</sub>C(OH)-psoralene. Occurs as a glucoside, *nodakenin*, C<sub>20</sub>H<sub>24</sub>O<sub>8</sub>·H<sub>2</sub>O, m.p. 218–219°, [α]<sub>D</sub> +56.6° in water. Acid hydrolysis yields nodakenetin, m.p. 192° (185°), [α]<sub>D</sub> –22.4°; *acetyl deriv.*, m.p. 130° (see Arima, Bull Chem. Soc. Japan, 1929, 4, 113; Späth and Tyray, Ber. 1939, 72 [B], 2089).

Nodakenin v. Nodakenetin.

Ostruthol, C<sub>21</sub>H<sub>22</sub>O<sub>7</sub>,

5-MeCH:CMC·CO·O·CMe<sub>2</sub>·CH(OH)CH<sub>2</sub>·O-psoralene, m.p. 137°, [α]<sub>D</sub><sup>15</sup> –18.3° in pyridine; *acetyl deriv.*, m.p. 125° (see Späth and Christiani, *ibid.* 1933, 66 [B], 1160).

Oxypeucedanin, C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>,



psoralene, m.p. 142–143°; *hydrate*, m.p. 134° (see Späth and Klager, *ibid.* 1933, 66 [B], 914).

Peucedanin, C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>, 4'-methoxy-5'-isopropylpsoralene, m.p. 109° (96°). Inhibits fermentation (see Späth and Klager, *ibid.* 1933, 66 [B], 749).

Phellopterin, C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>, 5-methoxy-8-Me<sub>2</sub>C:CH·CH<sub>2</sub>·O-psoralene. Occurs in *Angelica glabra* Makino and *Phellopterus littoralis* Benth., m.p. 102° (see Noguti and Kawanami, J. Pharm. Soc. Japan, 1941, 61, 77).

Psoralene, C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>, *fiscusin* [II (a)], m.p. 171° (162°) (see Späth et al., Ber. 1937, 70 [B], 73).

Xanthotoxin, C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>, *xanthotoxol methyl ether*, 8-methoxy-psoralene. Occurs in the seeds of *Angelica archangelica* Linn., m.p. 146° (see Späth and Pailer, *ibid.* 1936, 69 [B], 767).

Xanthotoxol, C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>, 8-hydroxy-psoralene, m.p. 252–253°. *Methyl ether v. xanthotoxin* (see Späth and Vierhapper, *ibid.* 1937, 70 [B], 248).

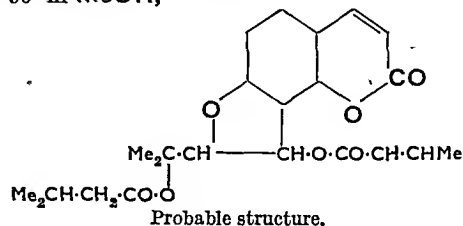
An unnamed coumarin, C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>, m.p. 183–184°, occurs in the fruit of *Seseli indicum* Wight and Arn. It is probably a methoxy-psoralene (see Bose and Guha, Sci. and Cult. 1936, 2, 326).

## II (b) 2':3':8:7-Furanocoumarins.

### Derivatives of Angelicin.

Angelicin, C<sub>11</sub>H<sub>6</sub>O<sub>3</sub>, *isopsoralene*, m.p. 142° (see Späth and Pailer, Ber. 1935, 68 [B], 940; Jois and Manjunath, *ibid.* 1937, 70 [B], 431).

Athamantin, C<sub>24</sub>H<sub>30</sub>O<sub>7</sub>, m.p. 59–60°, [α]<sub>D</sub><sup>22</sup> +96° in MeOH,



Occurs in *Peucedanum oreoselinum* Moench. (*Athamanta oreoselinum* Linn.) (see Späth *et al.*, *ibid.* 1940, 73 [B], 709, 1309).

isoBergapten,  $C_{12}H_8O_4$ , 5-methoxyangelicin, m.p.  $224^\circ$  (see Späth and Kubiczek, *ibid.* 1934, 70 [B], 1253).

isoPsoralene *v.* Angelicin.

Pimpinellin,  $C_{13}H_{10}O_5$ , 5:6-dimethoxyangelicin, m.p.  $119^\circ$  (see Wessely and Kallab, *Monatsh.* 1932, 59, 161).

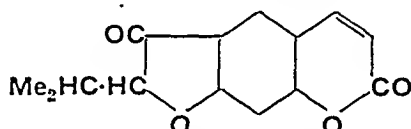
Sphodin,  $C_{12}H_8O_4$ , 6-methoxyangelicin. Occurs in *Heracleum sphondylium* Linn., m.p.  $189-191^\circ$  (see Späth and Schmid, *Ber.* 1941, 74 [B], 595).

Sphondylin,  $C_{12}H_8O_4$ , methoxyangelicin (?). Occurs in *Heracleum sphondylium* Linn., m.p.  $161-163^\circ$  (see Späth and Schmid, *ibid.* 1941, 74 [B], 595).

### Oroselone and Oreoselone.

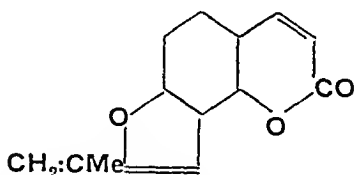
A few degradation products of natural coumarins have been described in the literature which have not, so far, been found in plants. Two different substances have been given the name "oreoselone." Späth now proposes to call one of them "oreoselone."

1. Oreoselone,  $C_{14}H_{12}O_4$ , a psoralene derivative,



obtained from peucedanin by acid hydrolysis, m.p.  $177-178^\circ$  (see Späth, Platzer, and Schmid, *ibid.* 1940, 73 [B], 709; Bruckhausen and Hoffmann, *ibid.* 1941, 74 [B], 1584).

2. Oreoselone,  $C_{14}H_{10}O_3$ , an angelicin derivative,



obtained from athamantin by acid hydrolysis, m.p.  $188-189^\circ$  (see Späth *et al.*, *ibid.* 1940, 73 [B], 709).

### III. THE PYRENOCOUMARINS.

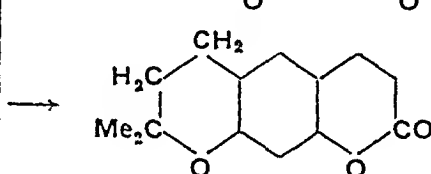
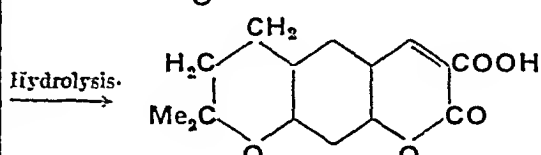
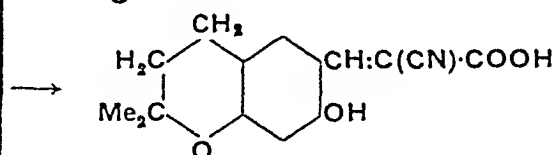
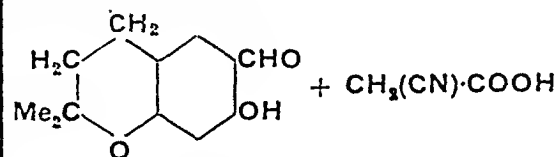
The pyrenocoumarins are few in number and all the known natural products are (a) 6':6'-

dimethyl-2':3':7:6-, (b) 6':6'-dimethyl-2':3':5:6- or (c) 6':6'-dimethyl-2':3':7:8-pyrenocoumarins (see p. 445a).

These compounds are also fish poisons and insecticides.

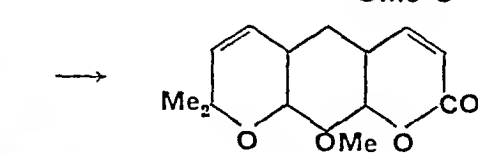
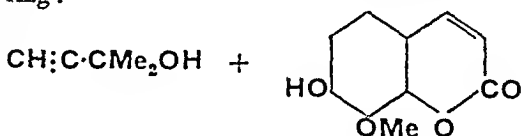
#### Synthesis.

1. From a chroman derivative by completing the  $\alpha$ -pyrone ring:



Dihydroxanthyletin.

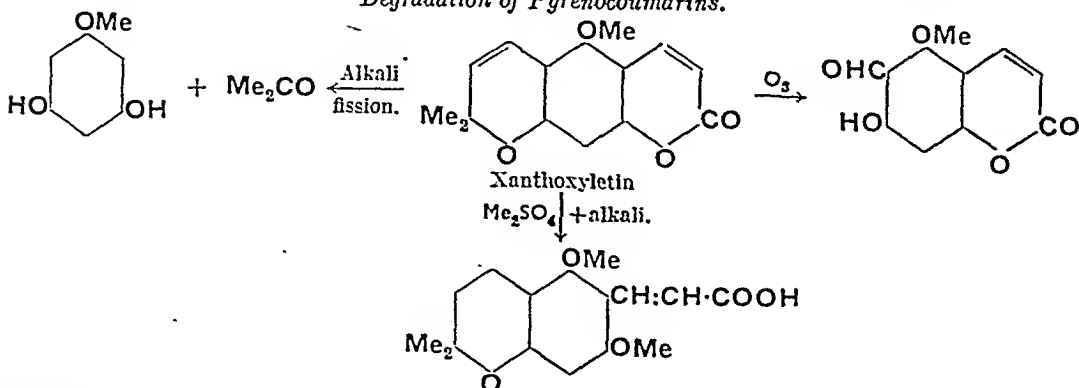
2. From a coumarin derivative by addition of an unsaturated compound to complete the pyren ring:



Luvangetin.

Angular compounds of types III (b) and (c) have also been synthesised by similar reactions.

#### Degradation of Pyrenocoumarins.







**NEOARSPHENAMINE.** (Mainly) sodium 3:3'-diamino-4:4'-dihydroxyarsenobenzene-N-methylenesulphoxylate. "*Neo-salvarsan*"; "*Novarsenobillon*." Used in treatment of syphilis. B.P., B.P.C. (v. Vol. I, 492a, and SYNTHETIC DRUGS).

S. E.

**NEODYMIUM.** Sym. Nd. At. no. 60. At. wt. 144.27 (Hönigschmid, Naturwiss. 1937, 25, 701); determined by comparison with pure silver, the previously accepted value of 144.26 obtained by Baxter, Whitcomb, Stewart, and Chapin (J. Amer. Chem. Soc. 1916, 38, 302) thus being confirmed; see also J.C.S. 1939, 351. Isotopes: Aston detected five isotopes by mass spectrographic analysis (Nature, 1933, 132, 930). They are of the following masses, given in order of abundance: 142, 144, 146, 143, 145, from which a value of 143.5 was obtained for the atomic weight. Later Dempster detected isotopes of masses 148 and 150 (Physical Rev. 1937, [ii], 51, 289), which leads to a calculated atomic weight of 144.29 (Mattauch and Hauk, Naturwiss. 1937, 25, 780).

Neodymium is a metallic element and a member of the cerium group of rare earths. Chemically it is very similar to lanthanum and praseodymium, separation from the latter being exceedingly difficult.

**Sources.**—Except for cerium, neodymium is the most abundant of the rare-earth elements. It occurs in almost all of the cerium ores, of which the most common are those named below. *Cerite*,  $\text{Ce}_3(\text{Ca,Fe})\text{H}_2\text{Si}_2\text{O}_{13}$ , chiefly from Sweden, was the principal source before the discovery of *monazite sand*,  $(\text{Ce,Y})\text{PO}_4 \cdot \text{ThO}_2 \cdot \text{SiO}_2$ , occurring chiefly in Brazil, Carolina, Bohemia, Australia, and the Urals; *monazite* is also known as *mengite*, *urdite*, and *edwardsite*. *Orthite*, *allanite*, or *xanthorite*,  $(\text{Cu,Fe})_2(\text{Al,Ce})_3\text{HSi}_2\text{O}_{13}$ , contains 10–20% of rare-earth oxides, chiefly of the cerium group. Radioactive *monazite sand* was discovered in Japan (Shibata and Kimura, Japan. J. Chem. 1923, 2, 1), containing  $\text{Nd}_2\text{O}_3$  20,  $\text{Ce}_2\text{O}_3$  20, and  $\text{Dy}_2\text{O}_3$  3.5%. A crystalline variety with a somewhat lower neodymium content was also found. Neodymium is also found in Norway, Canada, and Madagascar.

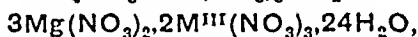
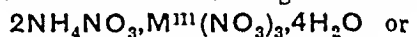
**Extraction and Separation.**—The finely ground ore is attacked by concentrated hydrochloric or sulphuric acid, and the aqueous extract treated with hydrogen sulphide to remove lead, copper, tin, bismuth, and similar metals. Alternatively, the ore may be fused with potassium bisulphate or sodium hydroxide, and the melt then digested with acid. Boiling oxalic acid solution is then added slowly to the boiling extract, giving a precipitate of the crude oxalates. Zirconium and thorium are removed by repeated treatments with boiling ammonium oxalate solution in which the rare-earth oxalates are almost insoluble. If large quantities of thorium are present, the neutral or very slightly acid solution of crude rare-earth salts may be treated with hydrogen peroxide, which precipitates an insoluble per-compound of thorium.

Ores containing relatively large quantities of niobium or tantalum are fused with potassium bifluoride, or treated with hydrofluoric acid to

extract these metals as their soluble fluorides or complex fluorides.

The crude oxalates are usually separated into the cerium, terbium, and yttrium groups by the James method; the dried oxalates are mixed with a small quantity of concentrated sulphuric acid, and the anhydrous sulphates then formed are dissolved in ice-cooled water. Solid sodium or potassium sulphate is added slowly to precipitate the least soluble sulphates, i.e., those of the cerium group. The separation is not sharp and the sulphates of the terbium group begin to precipitate before the precipitation of the cerium group sulphates is complete. This treatment is applied after preliminary fractional crystallisation of the nitrates if less than 15% of yttrium earths is present; under such circumstances the yttrium earths are concentrated in the more soluble nitrate fractions, and they are removed by the above procedure only when they have become abundant enough to interfere with the separation of the cerium group. Cerium is easily removed by oxidising a neutral solution with potassium bromate or permanganate, and boiling to precipitate a basic quadrivalent cerium salt.

The remaining elements are separated by fractional crystallisation (see RARE EARTHS). The double ammonium or magnesium nitrates,



are generally used to give a mixture of the praseodymium and neodymium salts. The fractionation is then continued, using the manganese double nitrates, the praseodymium salt being the less soluble. Other methods which have been used successfully to separate these two elements are the crystallisation of (i) the oxalates from nitric acid; (ii) the double carbonates; (iii) the *m*-diinitrobenzoates; and (iv) the simple nitrates from concentrated nitric acid. The fractional precipitation of the chlorides by gaseous hydrogen chloride has also been adopted.

**Preparation and Properties.**—The metal is prepared either by the reduction of the oxide or chloride, or by the electrolysis of a fused salt. The electrolysis of the chloride is usually carried out at high current-density using a finely divided carbon cathode (Matignon, Compt. rend. 1900, 131, 891; Sieverts and Roell, Z. anorg. Chem. 1926, 150, 261). The graphite cell is usually lined with molybdenum or tungsten. The effect of current density and neodymium oxide has been investigated by Kremers (Trans. Electrochem. Soc. 1925, 47, 350). Trombe describes a miniature cell using a molybdenum rod cathode (*ibid.* 1934, 66, 57) and Drossbach (Z. Elektrochem. 1938, 44, 124) has designed a cell with an iron wire cathode for the electrolysis of fused  $2\text{KCl}, \text{NdCl}_3$  at 860°C. using small currents. Impure neodymium was obtained by the reduction of the chloride with sodium (Matignon, Compt. rend. 1900, 131, 837), and Bommer and Hohmann (Z. anorg. Chem. 1941, 248, 357), using the method of Klemm and Bommer, have prepared pure neodymium by reduction of the chloride, *in vacuo*, with potassium.

When pure the metal is silver-white, but it normally possesses yellow streaks due to slow atmospheric oxidation.  $\rho_4^{20}=6.956$ ; at. vol. =20.62 c.c. The paramagnetic moment recorded by Trombe (Compt. rend. 1934, 198, 1591) of 17.8 Weiss magnetons agrees with the value obtained for its salts, and also with that calculated for the  $\text{Nd}^{+++}$  ion, i.e., 18 magnetons (Trombe, Ann. Physik, 1937, [v], 7, 385). The magnetic susceptibility, which is approximately equal to that of praseodymium, europium, and ytterbium, is  $39.51 \times 10^{-6}$  C.G.S. units (Trombe, Compt. rend. 1934, 198, 1591). An earlier value of  $36.21 \times 10^{-6}$  C.G.S. units was recorded by Owen (Ann. Physik, 1912, [iv], 37, 666). The susceptibility has been discussed theoretically by Selwood (J. Amer. Chem. Soc. 1933, 55, 3161) and Foex and Fehrenbach (Compt. rend. 1936, 203, 857).

The two reduction potentials of  $-1.870$  and  $-1.960$  v. have been determined by Noddack and Brukl (Angew. Chem. 1937, 50, 362). Neumann and Richter obtained the normal hydrogen electrode potential of  $1.748$  v. Like praseodymium, metallic neodymium has a hexagonal close-packed structure,  $a=3.655$  Å.;  $c=5.880$  Å.; atomic radius= $1.819$  Å. (Klemm and Bommer, Z. anorg. Chem. 1937, 231, 138).

It was suspected for a long time that neodymium is weakly radioactive, but it is now thought that such activity is due to impurities.  $\beta$ -Radioactive isotopes corresponding to the following masses have been prepared by neutron or deuteron bombardment of neodymium: 141, 151, and either 147 or 149.

**Spectra.**—The arc spectrum has been investigated by Joye (Arch. Sci. phys. Nat. Genève, 1913, 36, iv, 41) and Muthmann, Weiss, and Heramhof (Annalen, 1907, 355, 165); for the spark spectrum, see Exner and Haschek (Sitzungsber. Akad. Wiss. Wien, 1899, 103, IIa, 1071), Azcona (Chem. Zentr. 1941, I, 330), and Albertson, Harrison, and McNally (Physical Rev. 1942, [ii], 61, 167).

The absorption spectrum of neodymium salts in solution has been the subject of many investigations. The  $4,691$  Å. band coincides with a band of the praseodymium spectrum. Quill, Selwood, and Hopkins (J. Amer. Chem. Soc. 1928, 50, 2929) have stated that Beer's law does not hold for solutions of the chloride and nitrate. Selwood (*ibid.* 1930, 52, 4308) has studied the effect of concentration on the wavelength of these bands. Gardiner (*ibid.* 1926, 129, 1518) investigated the ultra-violet spectrum. For spectra in non-aqueous media, see Jones and Guy (Physikal. Z. 1912, 13, 649); Jones and Anderson (Proc. Amer. Phil. Soc. 1908, 47, 276); Jones and Strong (Amer. Chem. J. 1911, 45, 1; 1912, 47, 27); Schaffer (Physikal. Z. 1906, 7, 822).

**Uses.**—Neodymium and its compounds are used widely to a very limited extent. The total annual consumption is approximately 80 tons. The metal is sometimes deposited in the carbon cores of arc-light pencils, which produce intense white light. A mixture of neodymium and praseodymium nitrates is used for stamping trade marks on gas mantles and the like.

Neodymium is present to the extent of 15% in "mischmetal" (v. Vol. II, 516b). This alloy possesses interesting pyrophoric properties and is used widely in cigarette lighters, flash powders, tracer bullets, etc. Several alloys of chromium, nickel, aluminium, and magnesium, containing neodymium, have been patented in the past ten years for specific uses. Several of the salts are used in glass manufacture and pottery to impart delicate tints. The phosphate imparts a rose tint to porcelain, and the oxide a special bluish-red colour to glass. The subject is discussed fully by Schmidt (Glashütte, 1941, 71, No. 8, 105).

#### COMPOUNDS OF NEODYMIUM.

Neodymium is trivalent in all its compounds, although oxides approximating to the formulae  $\text{NdO}_2$  and  $\text{Nd}_4\text{O}_9$  have been reported (Brauner, Z. anorg. Chem. 1902, 32, 1; Marc, Ber. 1902, 35, 2382). The salts are pink or violet in the solid state, and usually pink in solution, giving characteristic absorption spectra (*see above*).

**Neodymium Oxide,  $\text{Nd}_2\text{O}_3$ .**— $p$  7.24. A clear blue powder with a pale red fluorescence, prepared by heating the hydroxide, oxalate, nitrate, or carbonate. It occurs in two forms: (a) blue-violet plates belonging to the trigonal trapezohedral system, obtained by heating the hydroxide or nitrate to  $1,100$ – $1,300^\circ\text{C}$ . for 1–2 hours, and (b) a pseudo-trigonal form prepared by heating the hydroxide at  $1,300^\circ\text{C}$ . for 5 minutes or the sulphate at  $1,000^\circ\text{C}$ . for several hours. The oxide is an exceedingly stable compound with a heat of formation of  $435$  kg.-cal. The solubility in water is  $5.7 \times 10^{-6}$  g.-mol. per l. at  $29^\circ\text{C}$ . Neodymium oxide is readily soluble in dilute acids.

**Neodymium Hydroxide,  $\text{Nd}(\text{OH})_3$ ,** is precipitated by the action of alkali on neodymium salts, as a bluish precipitate, although it has been obtained as a rose-coloured product. On heating at  $300$ – $350^\circ\text{C}$ . greyish-brown

#### $2\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

is formed, which is converted into  $\text{Nd}_2\text{O}_3 \cdot \text{H}_2\text{O}$  at  $525^\circ\text{C}$ . The hydroxide, like the oxide, is readily soluble in dilute acids.

**Neodymium Fluoride,  $\text{NdF}_3$ ,** may be obtained by the action of fluorine on a heated neodymium salt, or as a gelatinous precipitate by the addition of concentrated hydrofluoric acid to a solution of a neodymium salt (Popovici, *ibid.* 1908, 41, 634).

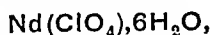
**Neodymium Chloride,  $\text{NdCl}_3$ .**—M.p.  $785^\circ$ ,  $p$  4.16. Obtained in the dry state by heating the hydrated chloride or oxide in hydrogen chloride or by the action of the chlorides of sulphur or carbon tetrachloride on the heated oxide. The heat of formation is  $249.4$  kg.-cal. The molten salt is green, depositing large violet prisms on cooling. The anhydrous salt is very hygroscopic and dissolves in water with a high heat of solution (3 kg.-cal.), the resulting solution being feebly hydrolysed. The conductivity has been studied by Bödlander (Dissert., Berlin, 1915, p. 13). The boiling-point of an alcoholic solution has been used to determine the molecular weight.

$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\rho_4^{12}$  2.282, is obtained from aqueous solution. The solubility is very high (246.2 g. per 100 g. of water at 13°C.) and the salt melts at 124°C.

Ammonia forms several addition compounds, with from one to twelve molecules of ammonia per neodymium chloride molecule (Matignon and Trannoy, *Compt. rend.* 1906, 142, 1042). Alcohol and pyridine form addition compounds,  $\text{NdCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$  and  $\text{NdCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ .

Neodymium Oxychloride,  $\text{NdOCl}$ , is formed by heating the chloride in water vapour or in air. The small mauve cubic crystals do not melt at 1,000°C.

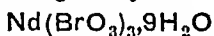
Neodymium Perchlorate,



is a very deliquescent violet-rose coloured product obtained by evaporating a solution of the oxide in perchloric acid, and allowing the solution to stand over concentrated sulphuric acid. At 170°C. the anhydrous salt is formed, but above 180°C. decomposition takes place. The spectrum has been studied fully by Selwood (*J. Amer. Chem. Soc.* 1930, 52, 3112).

Neodymium Bromide,  $\text{NdBr}_3$ , is prepared in the anhydrous state by the methods used to prepare the chloride, the red crystalline product being isomorphous with the chloride. The salt dissolves in alcohol and acetone and is slightly hydrolysed by water. The hydrates  $\text{NdBr}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NdBr}_3 \cdot 9\text{H}_2\text{O}$ , analogous to those of praseodymium bromide, are formed.

Neodymium Bromate,  $\text{Nd}(\text{BrO}_3)_3$ .—The anhydrous salt is obtained by heating  $\text{Nd}(\text{BrO}_3)_3 \cdot 2\text{H}_2\text{O}$  at 150°C.; the dihydrate is formed by heating the hydrate



to 100°C. The latter forms hexagonal prisms, very soluble in water, prepared by evaporation of the solution obtained by the addition of barium bromate to neodymium sulphate.

Neodymium Iodide,  $\text{NdI}_3$ .—This is a highly exothermic compound prepared by the action of hydrogen iodide on neodymium chloride near its melting-point, or by direct union of the two elements. At high temperatures an allotropic modification is formed.

Neodymium Sulphide,  $\text{Nd}_2\text{S}_3$ .— $\rho$  5.34, mol. vol. 72.1 c.c. A brown powder formed by the action of hydrogen sulphide on the anhydrous chloride or sulphate at 600–1,000°C. At higher temperatures a green vitreous mass results. Water readily decomposes the sulphide, but heat has no action below 2,200°C.

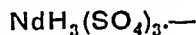
Neodymium Sulphite,  $\text{Nd}_2(\text{SO}_3)_3 \cdot \text{aq.}$ , is produced by passing sulphur dioxide into a suspension of neodymium hydroxide in water.

Neodymium Sulphate,  $\text{Nd}_2(\text{SO}_4)_3$ .—Prepared in the anhydrous state by heating the oxide and concentrated sulphuric acid gradually to red heat. It forms rose-coloured needles, exceedingly soluble in water. The ionisation has been considered by Aufrecht (*Dissert.* Berlin, 1904, p. 67) and Böldander (*ibid.* 1915, p. 33). The crystals decompose at 700–800°C. The heat of formation is 57.2 kg.-cal., and the heat of solution 36.5 kg.-cal. Several hydrates have been isolated:  $\text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  crystal-

lises on evaporating an aqueous solution. It loses the water of crystallisation at 350°C.  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is formed by adding sulphuric acid to a solution of neodymium nitrate and precipitating with alcohol. The resulting red prisms are isomorphous with the corresponding erbium, yttrium, and praseodymium salts. Extensive studies have been made on the solubility of this salt in water (Reinäcker, *J.C.S.* 1930, 1687; Friend, *ibid.*, p. 1633). Friend has attributed a break in the solubility curve to an allotropic modification; he has also prepared  $\text{Nd}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$  by the addition of the finely powdered octahydrate to dilute sulphuric acid between 0 and 30°C. At ordinary temperatures this readily passes into the octahydrate.

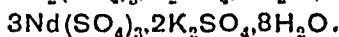
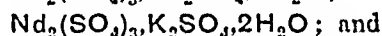
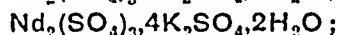
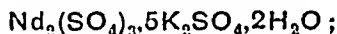
Neodymium Basic Sulphate,  $\text{Nd}_2\text{O}_3 \cdot \text{SO}_3$ , or  $(\text{NdO})_2\text{SO}_4$ , prepared by heating the anhydrous salt to 800°C. in air, is a bluish-red insoluble powder.

Neodymium Hydrogen Sulphate,



This salt forms clear rose-coloured needles, very similar to the corresponding praseodymium salt, and is obtained by evaporating a solution of the oxide in concentrated sulphuric acid.

Neodymium Double Sulphates.—The following have been prepared:



Some of these double sulphates show considerable differences from the corresponding praseodymium salts. For example,



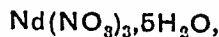
forms beautiful violet crystals, and a similar rubidium salt has been isolated. The thallium double sulphates have been studied.

Neodymium Selenide,  $\text{Nd}_2\text{Se}_3$ , is formed by the action of hydrogen selenide on the heated oxide or chloride, as a dark violet powder, insoluble in water. The properties are discussed fully by Klemm and Koczy (*Z. anorg. Chem.* 1937, 233, 84).

Neodymium Selenates,  $\text{Nd}_2(\text{SeO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Nd}_2(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$ , are prepared in the same way as the sulphates and are very similar. There is evidence for the existence of  $\text{Nd}_2(\text{SeO}_4)_3 \cdot 12\text{H}_2\text{O}$  (Friend and Round, *J.C.S.* 1928, 1820).

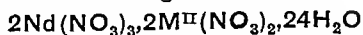
Neodymium Nitride,  $\text{NdN}$ , is a black powder, readily decomposed in humid air with the liberation of ammonia. It may be prepared by heating the metal at 900°C. or the carbide at 1,200°C. in nitrogen.

Neodymium Nitrate,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .—This hydrate and the pentahydrate,



are isomorphous with the corresponding bismuth compounds. These hydrates are prepared by adding the oxide to nitric acid and crystallising the solution. Many double nitrates are formed.  $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$  forms

reddish-violet plates (m.p.  $47^{\circ}\text{C}.$ ). In addition a series of salts of the general formula



has been prepared, where  $\text{M}^{\text{II}} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{or Cu}$ . These have been investigated fully from the point of view of separating the rare earths (Jantsch and Widgorow, *ibid.* 1911, 69, 222; Prandtl and Duerue, *ibid.* 1926, 150, 105; Friend, J.C.S. 1930, 1903).

**Neodymium Phosphates.**— $\text{NdPO}_4$  is formed by the fusion of microcosmic salt,  $\text{NH}_4\text{NaHPO}_4$ , and neodymium oxide, or by the addition of phosphoric acid to neodymium sulphate. An acid phosphate and the metaphosphate  $\text{Nd}(\text{PO}_3)_3$  are also known.

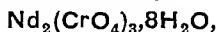
**Neodymium Carbide,  $\text{NdC}_2$ ,** in the form of golden yellow microcrystalline hexagonal plates, is obtained by heating a mixture of neodymium oxide and sugar charcoal in the electric furnace. Water reacts at room temperature to produce a mixture of gases, acetylene being the chief constituent.

**Neodymium Carbonate,  $\text{Nd}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ,** is obtained when carbon dioxide is passed into a solution of a neodymium salt in sodium bicarbonate solution. The hydrate loses six molecules of water over concentrated sulphuric acid, and the monohydrate is produced at  $100^{\circ}\text{C}.$  The basic carbonate  $\text{Nd}(\text{OH})\text{CO}_3$  is formed on boiling a suspension of the carbonate. Double salts are formed with potassium, sodium, and ammonium carbonates, and thallium double carbonates have been reported.

**Neodymium Boride,  $\text{NdB}_6$ .**—A product approximating to this composition has been obtained by electrolysis a mixture of neodymium and boric oxides with some lithium oxide and fluoride (Andrieux, Ann. Chim. 1929, [x], 12, 473). It forms blue crystals and resembles lanthanum boride.

**Neodymium Borates.**— $\text{Nd}_2\text{B}_4\text{O}_9$  is precipitated as a reddish-brown powder by the addition of borax to a solution of a neodymium salt. The orthoborate,  $\text{NdBO}_3$ , a violet-red microcrystalline powder, and the compound  $\text{Nd}(\text{BO}_2)_3$ , also exist.

**Neodymium Chromate,**



is formed by mixing neodymium oxide with a 0.1N. solution of potassium chromate in the minimum quantity of chromic acid. Brownish-yellow microscopic needles are formed.  $\text{Nd}_2(\text{CrO}_4)_3 \cdot 10\text{H}_2\text{O}$  is formed by double decomposition of neodymium nitrate and potassium chromate as a voluminous yellow precipitate. The anhydrous salt is prepared by fusion of the anhydrous chloride with potassium chromate.

**Neodymium Acetate,**



This forms violet-red flakes when the oxide is added to excess acetic acid. It is recrystallised from water. Many double compounds are formed with organic acetates.

**Neodymium Oxalate,  $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ ,** is precipitated by the addition of oxalic acid or an alkaline oxalate to a neodymium salt in

acid or neutral solution. It is a rose-coloured salt, relatively insoluble in water (1.48 mg. per l. at  $25^{\circ}\text{C}.$ ).

A. J. E. W. and R. F. H. **NEON.** Sym. Ne. At. no. 10. At. wt. 20.183 (International Atomic Weight Commission, 1934; Baxter and Starkweather, Proc. Nat. Acad. Sci. 1928, 14, 57, obtained the value 20.182 from density measurements). Isotopes: 20, 21, 22, with percentage abundances 90.00, 0.27, and 9.73, respectively (Bainbridge, Physical Rev. 1933, [ii], 43, 424; Vaughan, Williams, and Tate, *ibid.* 1934, [ii], 46, 329). Neon was the first inert element for which the existence of isotopes was discovered (J. J. Thomson, Proc. Camb. Phil. Soc. 1914, 17, 201).

#### ISOLATION OF NEON.

After the discovery of helium and argon it appeared probable that other gases with similar properties might exist to occupy vacant places in the periodic classification of the elements. In 1896 Ramsey and Travers began a search for them (see M. W. Travers, "The Discovery of the Rare Gases," London, 1928). In June, 1898, 15 l. of argon, prepared from air by chemically removing the nitrogen and oxygen, were liquefied by means of a new refrigerant, liquid air, supplied by Hampson who had just previously succeeded in preparing large quantities by throttle expansion of compressed air. The first portions of the gas which boiled off this liquid argon were collected separately and examined spectroscopically. The spectrum showed the presence of argon, helium, and a hitherto unknown gas, which was named neon.

A further quantity of the neon concentrate was then prepared in a different manner. A Hampson air liquefier was operated in a closed circuit, the gas leaving the liquefier being returned to the compressor, so permitting a continuous concentration of the lighter constituents in the unliquefied air. Some of this latter was condensed under pressure at liquid-air temperature, and then allowed to evaporate while being thoroughly agitated. The gas obtained in this manner was mainly nitrogen. After removing the nitrogen chemically, the residue was much richer in neon than the concentrate obtained from the 15 l. of argon prepared a year earlier. The helium-neon-argon mixtures obtained by the two processes were mixed.

To isolate the neon, Travers (*op. cit.*) used liquid hydrogen, prepared by himself for the purpose in an apparatus also utilising throttle expansion. At the boiling-point of liquid hydrogen ( $-253^{\circ}\text{C}.$ ), the argon and neon in the mixture were solidified, but not the helium, which has a boiling-point below that of hydrogen. The neon, with an appreciable vapour pressure at  $-253^{\circ}\text{C}.$ , was pumped away from the non-volatile argon, and after refractionation, gave the first pure neon ever prepared. Its density was found to be between 9.9 and 10.0.

To determine the amount of neon in air, W. Ramsey ("The Gases of the Atmosphere," London, 1915) admitted a measured quantity of air to a bulb containing coconut charcoal,

cooled to  $-100^{\circ}\text{C}$ . A large proportion of the oxygen and nitrogen was adsorbed, but not the helium and neon. The unadsorbed gases were pumped off and treated in the same manner with a smaller quantity of charcoal. The gas mixture then pumped off, still containing nitrogen and oxygen, was mixed with excess of oxygen and the nitrogen removed by sparking over sodium hydroxide solution. After removing oxygen by phosphorus, the mixture of neon and helium was admitted to a bulb containing charcoal cooled to  $-185^{\circ}\text{C}$ ., when the neon was completely adsorbed. The helium was pumped off, and when the charcoal warmed up the neon was collected and measured. Air was thus found to contain 12.4 vol. of neon in one million vol. of air, with 4.1 vol. of helium.

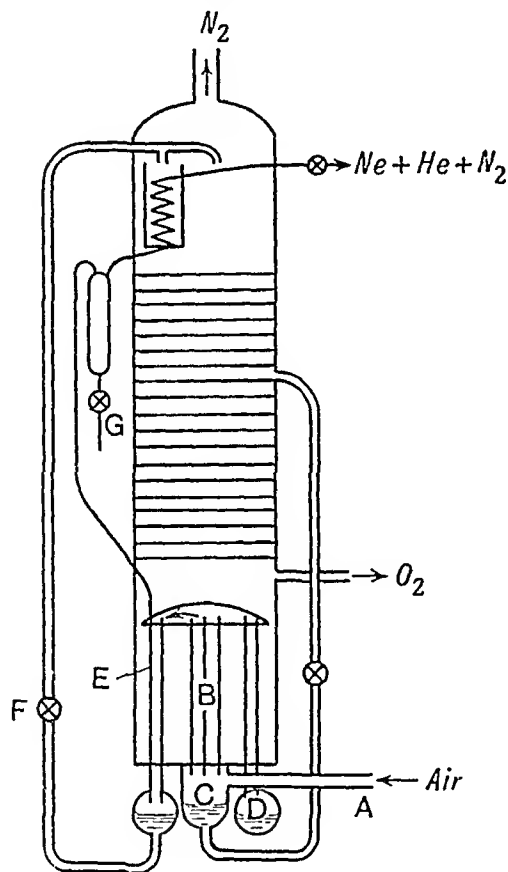


FIG. 1.

In 1909, G. Claude (*Compt. rend.* 1909, 148, 1454) found 15 vol. of neon (and 5 vol. of helium) per million of air, when experimenting with a plant treating 360 cu.m. of air per hour. Moureu (*ibid.* 1920, 171, 941) estimated 18 vol., and Watson (*J.C.S.* 1910, 97, 810) gave 18.2 vol. Recent work by G. H. Cady and H. P. Cady (*Ind. Eng. Chem.* 1945, 17, 760) supports the value 18 vol. per million.

The method employed by Claude for the extraction of neon and helium on an industrial scale is still utilised to-day. In his type of oxygen separator the air to be treated enters at A (Fig. 1) at a pressure of about 4 atm. and rises up the inner tubes, B, which are surrounded by liquid oxygen boiling at a pressure a little

above atmospheric. Part of the air is liquefied and drops back into the vessel C, this liquid having an oxygen content of about 40%. The uncondensed gases pass over to the outer tubes, where they condense to a liquid containing only a few per cent. of oxygen, and which collects in vessel D. Neon and helium, with boiling-points  $63^{\circ}\text{C}$ . and  $86^{\circ}\text{C}$ . lower than that of nitrogen, resist liquefaction and accumulate in the vapour above the liquid in vessel D. More nitrogen is liquefied on passage up tube E, and a further concentration of the rare gases is effected by connecting E to a coil immersed in the nitrogen-rich liquid coming from D; this is now subjected to a pressure a little above atmospheric, after passage through valve F, and therefore has a temperature some  $12^{\circ}\text{C}$ . lower than the liquid in D. The liquid nitrogen rising in the coil flows back, and is withdrawn through the valve G. From the top of the coil a gas mixture is withdrawn which may contain as much as 80% of helium-neon. In this mixture there is always a few per cent. of hydrogen, equivalent to 0.5-1.0 vol. per million vol. of treated air. Whether this hydrogen is a normal constituent of the atmosphere, or whether it arises from the oil used as a lubricant on the air compressor, has not been conclusively determined. After removing the hydrogen chemically, the nitrogen content is further reduced by sub-

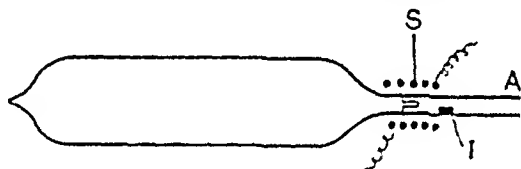


FIG. 2.

jecting the mixture at high pressure to a low temperature, produced, e.g., by liquid nitrogen boiling at atmospheric pressure. Finally, the mixture, having now a small nitrogen-content, is separated by adsorption on cooled active charcoal, with subsequent fractional desorption. Helium and neon are thus isolated in a very pure state. Minute traces of impurity render them useless for most of their applications, and great care has to be exercised in maintaining high purity. They are usually supplied in sealed glass containers at atmospheric pressure, having, for example, the form shown in Fig. 2.

To avoid contamination by the gases adhering to the glass surface, the container is heated to a high temperature whilst being evacuated, and is then washed out with some of the highly purified rare gas before cooling, final filling, and sealing off. The outlet tube of the container is closed by a thin walled glass partition. The container is fused to the user's equipment at A, and after evacuation up to A the partition is broken by causing the piece of iron I to strike it on passing a current through the solenoid S.

#### PROPERTIES OF NEON.

Neon is an inert, colourless, tasteless, odourless gas, which does not condense at the temperature of liquid air but is solid at the temperature

of liquid hydrogen. The solid forms a face-centred, cubic crystal, with a lattice constant of 4.52 Å. The atomic radius, calculated from ionisation potentials, is 0.68 Å. (Mazunder, Z. Physik, 1930, 66, 119).

The saturation vapour pressure above solid neon has been determined by Keesom and Haantjes (Physica, 1935, 2, 460):

$T(^{\circ}\text{K.})$	$p(\text{mm. Hg.})$
15.92	1.07
16.93	2.67
17.97	6.70
18.58	10.71
19.79	24.88
20.45	37.35

Crommelin and Gibson (Comm. Leyden No. 1856, 1927) quote data for the vapour pressure on which the following figures are based:

$T(^{\circ}\text{K.})$	$p$
15.46 (solid)	0.55 mm. Hg.
18.24	7.8
20.00	28.2
21.92	91
22.94	148
24.07	250
24.60	317
24.65	325
25.67	451.6
26.50	605.2
27.24	1.000 atm.
36.34	7.970 atm.
44.45	26.86 atm. (critical point).

(More recent data on vapour pressure are given in Rev. Mod. Physics, 1941, 13, 310.)

The gas density was determined by Baxter and Starkweather (Proc. Amer. Acad. 1928, 14, 50). They found a value of 0.89990, the correction for deviation from Avogadro's rule being given by:

$$1 + \lambda = 0.99941 \text{ (at } 0^{\circ}\text{)}.$$

The density of liquid neon is 1.248 at 24.58°K. (Kamerlingh-Onnes and Crommelin, Comm. Leyden No. 147d, 1916).

The normal boiling-point is 27.17°K. (−245.92°C.), and the melting-point (triple point) is 24.57°K. (−248.52°C.) at 323.5 mm. pressure (Crommelin and Gibson, Comm. Leyden No. 185b, 1927.)

The critical temperature of the gas has been given as 44.74°K., and the critical pressure 27.23 atm. (Verschaffelt, Comm. Leyden, 1928, 17, Suppl. 64d). A later determination (Woolsey, J. Amer. Chem. Soc. 1937, 59, 1577) gave 44.45°K. and 26.86 atm., respectively.

Neon gas has a refractive index of 0.006275 (for  $\lambda$  5462 Å.) with respect to vacuum at 0°C. (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1932, A, 135, 40).

The magnetic susceptibility at 20°C. is quoted as  $-7.651 \times 10^{-6}$ ; at  $-183^{\circ}\text{C.}$  it is  $-7.64 \times 10^{-6}$  (Havens, Physical Rev. 1933, [ii], 43, 992).

The thermal conductivity has been determined by Curie and Lepape (Compt. Rend. 1931, 193, 842), who found a value of 0.0001092 at 0°C.,

with respect to air, a value of 0.0000583 being assumed for air.

Keesom and Lammeren (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 614) give the following figures for the molar specific heat of neon gas:

$T(^{\circ}\text{C.})$	$p(\text{atm.})$	$C_p$
−245.3	1	5.55
0	0.88	4.96

Keesom and Haantjes (Physica, 1935, 2, 986) studied the thermodynamic properties of liquid and solid neon. They state that the specific heat of liquid  $^{20}\text{Ne}$  is greater than that of  $^{22}\text{Ne}$ , whereas this order is reversed for solid neon. The atomic heat of fusion of  $^{22}\text{Ne}$  is 1.18 g.-cal. greater than that of  $^{20}\text{Ne}$ . The calculated heat of fusion is 80 g.-cal. per g.-mol. This agrees with the value of 80.1 determined experimentally by Clusius (Z. physikal. Chem. 1936, B, 31, 459). Clusius quotes 3.26 units for the entropy of fusion.

The heat of vaporisation of liquid neon is quoted as 431.47 g.-cal. per g.-mol. at 25.17°K., and 415.31 g.-cal. per g.-mol. at 27.15°K. (Mathias Crommelin, and Kamerlingh-Onnes, Comm. Leyden No. 162b, 1923.) The calculated value from the Trouton-Nernst equation is 365 g.-cal. per g.-mol. at 27.17°K.

The viscosity of neon has been studied by Edwards (Proc. Roy. Soc. 1928, A, 119, 378). It increases with temperature, and has a value of  $3.076 \times 10^{-7}$  at 15°C.

Neon gives two main sets of spectra. The Ne I system (Paschen, Amer. Phys. 1919, 60, 405) corresponds to an ionisation potential of 21.47 v.; it is a singlet-triplet system, consisting of 132 series. The strongest lines lie in the visible and near ultra-violet. There is also a strong accumulation of lines in the orange region. The strongest line in the visible region is the  $D_2$ -line, at 5852.5 Å. (yellow). This spectrum is used for the detection of neon. The Ne II system is a doublet-quartet system corresponding to an ionisation potential of 40.9 v. (Russel, Compton, and Boyce, Proc. Amer. Acad. 1928, 14, 280); Frisch, Z. Physik, 1930, 64, 499).

There is also a possible Ne III system (ionisation potential 63.2 v., singlet-triplet-quintet) and a Ne IV system (doublet-quartet). Details of the spectra are given in H. Kayser, "Tabellen der Hauptlinien der Elemente," Berlin, 1926.

For neon absorption-lines in stellar spectra, see Menzel and Marshall (Cambridge Mass., Harvard Coll., Astr. Observatory, reprint 99). For the Zeeman effect of neon, see Murakawa and Iwana, Sci. Pap. Inst. Phys. Chem. Res. Tokyo, 1930, 13.

The dielectric properties of neon have been studied by Watson, Rao, and Ramaswamy (Proc. Roy. Soc. 1931, A, 132, 569). The dielectric constant  $\epsilon$  is given by  $(\epsilon - 1)_{25^{\circ}} \times 10^6 = 122.9$ . Neon has the smallest known value of dielectric cohesion,  $dV/dp$  (where  $V$ =striking potential,  $p$ =pressure) (Bouty, J. Physique, 1903, 2, 401; Ann. Chim. Phys. 1913, [viii], 28, 545). This makes it a useful medium for gas-discharge tubes.



## USES OF NEON.

Neon is extensively used in discharge tubes. A neon tube consists of a length of glass tube at each end of which a metal electrode is attached. It is filled with neon to a pressure of about 10 mm. of mercury. When a suitable voltage is applied across the electrodes a current passes through the gas, which glows and radiates light. Alternating current is used, the positive column starting out from each electrode; owing to the persistence of vision, the discharge presents a symmetrical appearance in the tube. High-tension current is necessary, the voltage ranging from 5,000 to 15,000, and current from 15 to 50 milliamp., whilst the tubes may be up to 60 ft. long. In a clear glass tube the glow is an attractive, warm orange-red. When a little mercury is present with the neon, the glow becomes blue; it appears green in a yellow glass tube. Such neon tubes run cold, and in cold weather the vapour pressure of mercury is insufficient to maintain the blue colour; this disadvantage is overcome by the addition of argon. Neon tubes have a luminous efficiency of 8-15 lumens per watt, much the same as that of a gas-filled tungsten-filament lamp.

If the electrodes are placed close together, the light emitted comes principally from the negative glow, the visible positive column and anode glow being entirely absent ("Osglim" lamp). Such "negative glow tubes" are made for use as low-power illuminants, as indicators to show whether a circuit is "live" or "dead," as a temperature standard for use with the disappearing-filament pyrometer, in sound-film recording, etc. They have a neon or helium-neon filling and operate on 200-250 v. supplies. The property that a discharge tube possesses, in virtue of which it remains effectively non-conducting until the applied voltage reaches a definite value, namely, the striking potential, permits of its use as a protective device in various electrical circuits.

Some of the radiation of low-pressure discharge-tubes is in the ultra-violet region, and is invisible. Substances exist which are capable of transforming ultra-violet radiation into radiation detectable by the eye, i.e., of transforming "invisible" energy into "visible" energy. Such luminescent substances are used to coat the interior walls of discharge tubes, either to change the effective colour or to improve the efficiency, and some of them can be excited by neon. Colours, suitable for interior lighting, may be produced at efficiencies comparable with those of the tungsten lamp.

Whereas high-tension current is required for cold-cathode tubes, ordinary 200-240-v. supplies will operate the more recently developed "hot-cathode" tubes. In these the electrodes consist of alkaline-earth oxides which are maintained in a hot, electron-emitting condition. High current-densities thus become possible, so that compact units of high luminous output are practicable, greatly exceeding in candle power cold-cathode lamps of the same dimensions. Tubes filled with neon at a few millimetres pressure radiate orange-red light with an efficiency considerably in excess of that afforded

by tungsten-filament lamps and coloured filters. Such tubes have found application as beacon lights on aerodromes and in lighthouses, on account of the high mist- and fog-penetrating power possessed by the neon light; they have also been employed in floodlighting and decorative lighting, and in horticulture where irradiation with red light is said to hasten the growth of plants.

Neon, and in part argon, are further used as filling gases for modern metal-vapour lamps. When the cold lamp is switched on, the rare gas allows passage of the current, which is later continued by the metal (sodium or mercury) after its vapour pressure has been raised sufficiently by heating the lamp.

C. R. H.

"NEONAL" 5-Ethyl-5-n-butylbarbituric acid. "Soneryl." Sedative and hypnotic. B.P.C. (v. SYNTHETIC DRUGS).

S. E.

NEONITE (v. VOL. IV, 519b).

NEOPINE (v. OPIUM).

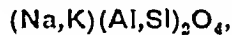
"NEOSTIBOSAN". Diethylamine *p*-amino-phenylstibinate. Used in treatment of Kala-azar. B.P.C. (v. SYNTHETIC DRUGS).

S. E.

NEOSYNEPHRINE HYDROCHLORIDE. 1- $\alpha$ -Hydroxy- $\beta$ -methylamino- $\alpha$ -*m*-hydroxyphenylethano hydrochloride. Vasoconstrictor-active when administered orally (v. SYNTHETIC DRUGS).

S. E.

NEPHELINE. A member of the feldspathoidal group of rock-forming minerals that form instead of feldspars in certain igneous rocks rich in alkalis and poor in silica. It is a sodium potassium aluminium silicate, essentially



the amount of potassium being usually low,  $\text{K}_2\text{O}$  not exceeding 7%; calcium may also be present. Artificial nepheline,  $\text{NaAlSi}_3\text{O}_8$ , contains  $\text{Na}_2\text{O}$  21.8,  $\text{Al}_2\text{O}_3$  35.9%. The natural mineral crystallises in the hexagonal system and occurs in two varieties. "Glassy" nepheline, found in recent soda-rich lavas, forms small colourless prismatic crystals, but the much more common "greasy" variety, often called *elvolite*, is nearly always massive or granular, is of a grey, greenish or reddish colour, and occurs in plutonic rocks, such as nepheline syenite. Nepheline fuses easily to a colourless glass, colours the flame a strong yellow, and is readily decomposed by acids with gelatinisation.  $\rho$  2.55-2.65, hardness 5½-6. It is rarely found in rocks that contain quartz. Extensive masses of nepheline-syenite occur in the Kola Peninsula, U.S.S.R. (locally associated with apatite), Norway, South Africa, and in the Bancroft district of Ontario where pegmatites often yield large masses of almost pure nepheline for industrial use.

During the past decade nepheline has been gaining favour at the expense of feldspar as a source of aluminium in the glass industry for addition to the glass batch. Most of the nepheline used in this way comes from Ontario, whose export of nepheline-syenite in 1940 amounted to about 20,000 tons. The Russians



utilise nepheline from Kola as a substitute for bauxite in the manufacture of metallic aluminium, and in various other industries including ceramics, leather, textiles, and rubber.

D. W.

## NEPHELOMETRY AND TURBIDIMETRY.

**Definitions and Scope.**—Nephelometry is usually taken to mean the photometric measurement of the light scattered by a medium such as a cloud or a suspension in a liquid. It should be distinguished from turbidimetry, which consists in the measurement of the light *transmitted* by such a medium. The transmission of a turbid medium is reduced because of the loss of light that is scattered, so that turbidimetry and nephelometry are complementary methods of examining the same phenomenon.

This distinction has not always been so clearly made, but definitions of turbidimetry and nephelometry on these lines have now been recommended by a committee appointed by the Society of Public Analysts (Analyst, 1942, 67, 164). The two types of measurement are made for similar purposes and by somewhat similar instruments, so that it is convenient to consider the two subjects together in this article.

A number of turbidimeters and nephelometers will be first described, and some of the relevant properties of scattering media will be mentioned; then reference will be made to a number of uses to which the methods of nephelometry and turbidimetry may be put.

**Turbidimeters.**—Any instrument that can be used for colorimetry (in the chemical sense) can also be used for turbidimetry. For example, the Duboscq colorimeter (*v. Vol. III, 303d*), the Pulfrich photometer (*v. Vol. III, 304d*), and the Lovibond tintometer (*v. Vol. III, 302b*) can be used for this purpose. Any of the various types of photoelectric colorimeter may also be used as turbidimeters; there are a number of types of such instruments on the market, and descriptions of several are given by Guild (J. Sci. Instr. 1938, 15, 65) and Muller (Ind. Eng. Chem. [Anal.], 1941, 13, 667).

A very simple turbidimeter of the visual type that may be used for turbidities of, say, natural or industrial water, consists of a column of liquid of adjustable depth, in a tube with a clear glass bottom, below which is a lamp. The depth of the column is increased until the lamp filament as seen through it just disappears, and conversely the depth is decreased until the filament just appears. The mean of the two depths of liquid then gives a measure of its turbidity. One such instrument is described by Parr and Staley (Ind. Eng. Chem. [Anal.], 1931, 3, 66).

**Nephelometers.**—In most nephelometers the light scattered from two specimens is compared. One of these is a standard, the other being a specimen under examination. The standard may be a plate of ground glass, etc., or other permanent material, but more often is a solution of the same type as the test specimen. In visual instruments, at least, the method of use is to adjust the intensity of the incident light (or, in some instruments, of the scattered light) for one of the specimens, until the two scattered beams are matched in intensity.

In one of the earliest forms two tubes were used with their axes coinciding at the observer's eye (Richards, Proc. Amer. Acad. Arts. Sci. 1894, 30, 385). The tubes were illuminated from the side, and the lengths of each tube illuminated were adjusted by sliding opaque sleeves up and down the tubes until the intensities of scattered light from the two tubes were judged to be equal.

Current forms of nephelometer based on this principle are analogous to the Duboscq type of colorimeter (*v. Vol. III, 303, Fig. 3*). In this case the walls of the cups are of clear glass and have black glass ends. The cups are illuminated from the side by a special lamp-house and viewed, as in the colorimeter, from the top.

The effective length of illuminated column is adjusted by means of the usual raising and lowering plungers, which must, in this case, have opaque sides with clear glass ends. Commercial forms of this nephelometer are usually arranged so that they can readily be converted into colorimeters.

A micro-form of this type of nephelometer has been described, which requires only 3–5 c.c. of liquid (Kleimann, Biochem. Z. 1923, 137, 148). In this the cylindrical cups holding the liquids under test are of small diameter and are immersed in rectangular glass cells of liquid, so that a uniform beam may be transmitted through the large curvature of the wall of the cup. To secure a sensitive measurement for small intensities of scattered light, it is necessary to ensure that the instrument is well provided with diaphragms, so that the field of view is only illuminated by the scattering solution under test, and that the effect of light scattered from the base or walls of the cups is reduced to a minimum. With this condition obtaining, a high intensity of illumination will help to give good sensitivity in comparing very small turbidities.

This latter principle was followed in a sensitive nephelometer which was specially designed for comparison of the light scattered by different optical glasses. In this instrument high-powered lens systems formed images of a carbon arc inside two glass specimens to be compared. These images were viewed in a direction at right-angles to that of the incident beams, and an adjustable aperture in one beam was used for matching the intensities of the two.

Several instruments have been described (Ind. Eng. Chem. [Anal.], 1935, 7, 262; J. Sci. Instr. 1939, 16, 99) which use one scattering solution only, and bring together into the two halves of a photometric field the light scattered by a solution and the light transmitted through it, respectively. An adjustable optical wedge (or similar device) in the transmitted beam serves to match the two halves of the field. In this way the ratio of transmitted to scattered light is measured. For a given increase in concentration of scattering material in a liquid, the scattered light is increased and the transmitted light reduced, so that the change in the ratio is greater than the change in either of the separate quantities determined by any of the previously described instruments. This instrument should therefore be particularly

useful in the determination of small changes of turbidity. It has the further advantage that no comparison standard is necessary in routine use of the instrument. (Of course standard solutions are required in initial calibration of this as of other instruments.)

The Pulfrich photometer (v. Vol. III, 305, Fig. 4) can be arranged with side illumination for specimen tubes, when it is required to be used as a nephelometer. In this case the intensity of one of the scattered beams is reduced by the adjustable aperture of the photometer.

Modern forms of the Lovibond Tintometer (see Fawcett and Howitt, J.S.C.I. 1939, 58, 342) may be used for nephelometry. The scattering solution, illuminated from the side and observed from the front, forms one half of the photometric field. The other half of the field is illuminated by light reflected from a magnesium oxido plate, which passes through a fixed neutral density to reduce its intensity suitably, and also through the Tintometer colour slides. Any colour difference in the two halves of the field is first corrected by the use of the colour slides, and then the intensities are matched by means of the "obturator" vane, the scale of which reads directly in densities.

The various photo-electric fluorimeters that have been designed (a number of these are described by Muller, Ind. Eng. Chem. [Anal.], 1941, 13, 667) may also be used as nephelometers.

**Rayleigh's Law of Scattering.**—Before proceeding further it will be convenient to state Rayleigh's equation for the intensity of scattered light, because, although of limited application, it forms a convenient starting point for discussing the properties of suspensions.

Rayleigh's law was deduced for the case of non-conducting particles that are small compared with the wave-length ( $\lambda$ ) of the incident light. This law may be stated as:

$$I_s/I_0 = \{(n' - n)/n\}^2 (1 + \cos^2 \beta) (\pi a^6 V / \lambda^4 r^2)$$

where  $I_0$  is intensity of the incident beam;

$I_s$  is the intensity of the light scattered at an angle  $\beta$  to the direction of incidence;

$a$  is number of particles per unit volume;

$V$  is the volume of a particle;

$r$  is the distance of the observer;

$n'$  is refractive index of suspended material;

$n$  is refractive index of medium.

The implications of this law in relation to nephelometric measurements will be developed in the following sections.

#### APPLICATIONS OF NEPHELOMETRY.

**Determination of Concentration.**—The most usual use for any of the nephelometers and similar instruments described above is for the determination of the concentration of an insoluble substance such as, for example, silver chloride. The method is not absolute, that is to say an instrument must first be calibrated by taking measurements with a series of known concentrations of the material in question. Since the measurements are affected by many

factors it is most essential that in all this work a technique should be carefully worked out that will give reproducible results, and that this technique should be then rigidly adhered to. A number of factors that influence these measurements and which will be discussed in turn are:

1. Solubility of the precipitate.
2. Nature of liquid.
3. Particle size.
4. Use of protective colloid.
5. Colour of the suspended material.

1. The sensitivity of the nephelometric method is in general limited, not by the sensitivity of the nephelometer, but by the solubility of the material in question. Thus, for example, the solubility of silver chloride in water is of the order of one part per million, so that in the estimation of chlorine nephelometrically as silver chloride a greater dilution than this cannot be detected; at higher concentrations, only a fraction of the chloride present is precipitated as silver chloride. Nevertheless, if calibration measurements are made on known solutions a curve can be prepared showing the relation between instrument reading and *total* chloride, not merely the portion in suspension. This curve can then be used for the analysis of unknowns prepared in exactly the same way as the standards. In this connection it must, of course, be remembered that the solubility of the silver chloride will be affected by the temperature and the nature and quantity of other materials in solution.

2. The nature of the liquid that holds the suspension is also a factor for consideration. Apart from the effect of variations of solubility with different liquids, as discussed above, the refractive index of the liquid (as also that of the suspended material), affects the intensity of scattered light. By Rayleigh's formula (above) the intensity of scattered light is greater the greater the difference of refractive index between suspension and liquid. Thus it has been found that the light scattered by a barium sulphate suspension in glycerin is less than that scattered by the same suspension in a mixture of glycerin and water.

3. It is seen from Rayleigh's law that for particles small compared with the wave-length of light, the scattered light is proportional to the number of particles and the square of the volume of a particle, i.e., to  $aa^6$ , where  $a$  is the diameter of a particle. But since the concentration (in units of mass) is proportional to  $aa^3$ , the scattering is proportional to the product of concentration and the cube of the particle size. Thus, at constant concentration, for very small particles (e.g., molecules in solutions) the scattering is small but increases very rapidly with increasing particle size.

When the particle is not small compared with the wave-length of the incident light, Rayleigh's law no longer applies. For particles large compared with the wave-length of light it is obvious that the scattering is proportional to the surface area of particles, i.e., to  $aa^2 = aa^3/a = \text{concentration/diameter}$ . In this range, therefore, for constant concentration the scattered light decreases with increasing radius. It is thus

obvious that there is some size or range of sizes in which the scattered light has a maximum intensity.

Owe (Kolloid-Z. 1923, 32, 73) made nephelometric measurements with barium sulphate suspension of varying sizes, and showed that for particles below  $0.5\mu$ . diameter the scattered light increased with increasing particle size, whereas for larger particles, of above  $1.0\mu$ . diameter, the scattering decreased with increasing diameter. The theory given above is thus confirmed, but unfortunately Owe does not show complete results for the range of sizes between  $0.5\mu$ . and  $1.0\mu$ . where neither of the above considerations apply.

It is therefore obvious that to obtain reliable nephelometric measurements of concentration, particle size must be controlled by proper methods of forming a suspension. Important factors in this connection are temperature, concentration of reagents, method of mixing, time between mixing and measurement, etc.

4. Colloidal solutions may be divided into two types: (a) emulsoids—known variously as hydrophilous, hydrophilic, gelatinising, etc.—which can exist in appreciable concentration without losing their colloidal nature; and (b) suspensoids, which are non-gelatinising, anhydrophilous, hydrophobic, etc., and which coagulate when their concentration is increased. Appreciable concentrations of suspensoids could not be used in nephelometric work but for the fact that the addition of a colloid of the emulsoid type will inhibit the coagulation. This added emulsion is known as a protective colloid. (In some cases where the two materials carry opposite electric charges, the added emulsoid may instead produce coagulation.) The general effectiveness of an emulsoid as a protective colloid is specified by its "gold number" (v. Vol. III, 287b). The gold number is determined by the effectiveness of an emulsoid in preventing the increase in particle size of a gold solution, which is indicated by the colour change from red to blue. Quantitatively the gold number is equal to the weight in milligrams of dry material which, added to 10 c.c. of gold sol. (concentration 0.0055%), is just sufficient to prevent the red-to-blue colour change on addition of 1 c.c. of 10% sodium chloride solution. Thus the smaller the gold number, the greater is the protective action of an emulsoid. Gold numbers for typical protective colloids are gelatin 0.005, gum arabic 0.15–0.25, potato starch 25.

5. The light scattered or transmitted by a solution being measured nephelometrically or turbidimetrically (respectively) will often be coloured. Owing to the selective effect of Rayleigh's law, according to which the scattering is proportional to  $\lambda^{-4}$ , the shorter wavelengths (blue) of a beam of white light will suffer greater scattering than the longer wavelengths (red), so that the scattered beam will appear bluish while the transmitted will be yellowish. In some cases the beams will be more definitely coloured, as in the case of gold solutions, for example, which are strongly coloured (Rayleigh's law does not apply in this case because the particles are electrically conducting). In the case of suspensions of larger

particle-size the materials may have their own characteristic colours, e.g., lead sulphide or potassium cobaltinitrite.

It is, of course, important that conditions of formation of the suspensions are so standardised that there is no variation of colour between one sample and another, otherwise results may not be comparable.

Another point to consider is the colour of the liquid in which the particles are suspended. Thus for example potassium may be estimated turbidimetrically as potassium cobaltinitrite by addition to a solution of a potassium salt of an excess of sodium cobaltinitrite. This latter is yellow, and it is important that the quantity used be definite, otherwise the transmission of the suspension will not depend only on the concentration of suspended material. In this example use of a red colour-filter in the measuring beam is a great advantage, because the yellow sodium salt in solution absorbs very little red light, so that the effect of variation in the concentration of this is then much less important.

*Standardisation.*—From all that has been said above, it is obvious that the essential of all nephelometric and turbidimetric work is the calibration of a method before use with the instrument to be used, and the standardisation of conditions so that the obtaining of reproducible results is ensured. Thus many workers limit themselves even to a definite manner of shaking a solution after mixing the components to ensure a suspension of reproducible particle-size.

A valuable example of the work required to determine the proper conditions for obtaining good nephelometric results, is to be found in a paper by Lamb, Carleton, and Meldrum (J. Amer. Chem. Soc. 1920, 42, 251) on silver chloride. All their measurements were made against a standard suspension of "kieselgühr" that had been allowed to stand for some days, so that coarse particles had settled out and no further change would take place during its use. The paper is concerned with the concentration of silver chloride that gives the best reproducibility of measurements with the particular nephelometer in use; this was found to be  $9 \times 10^{-5}$  M.

It was found that some time must elapse for the particles to grow to a stable size, during which time the opalescence increases. If the solution is left at room temperature, maximum opalescence is not reached for 60 minutes, but it is found that if the solution is heated to  $40^\circ\text{C}$ . for 30 minutes and then cooled, the opalescence has reached a maximum value; this does not afterwards decrease by further coagulation, except when stronger solutions are used ( $30 \times 10^{-5}$  M.), when it was found to be important to examine the solutions not longer than half-an-hour after cooling.

In the case of silver chloride, which is of course sensitive to light, it was found important to keep the solution in the dark, except during the actual measurement, otherwise the opalescence was found to be decreased.

*Determination of Particle Size.*—The variation of scattered light with particle size

has already been discussed, but this does not seem to have been used as a means of determining particle size. The complementary property, viz. variation of transmitted light with particle size, is being used, however, for this purpose. Consider a dilute suspension of opaque particles which are large compared with the wave-length of light; suppose there are  $n$  particles per c.c., each of diameter  $a$ . Consider a beam of light of intensity  $I$  traversing an element of the suspension of length  $dl$  in the direction of the beam and of unit area in a perpendicular direction. For a dilute suspension it can be assumed that the particles are not obscuring one another, and so the fraction of light stopped ( $dI/I$ ) by the particles is equal to the ratio of the projected area of the particles to the whole area of the beam, which is unity. Thus:

$$dI/I = (\pi a^2/4) n dl,$$

or, integrating over a fine length  $l$  of the suspension,

$$\log(I_0/I) = (\pi a^2/4) nl$$

where  $I_0$  and  $I$  are the intensities of the incident and emergent beams, respectively.

(It should be noted that a dilute suspension of opaque particles has been assumed, and the effect of light scattered by the particles emerging as part of the transmitted beam has been neglected. A considerable amount of work has been done on this subject, and it has been found that while the above equation holds in many cases, its validity should be checked for each particular type of particle.)

Measurement of the transmission of a suspension, by a suitable colorimeter or turbidimeter, thus allows a determination of  $na^2$ . By filtering and weighing the ratio  $na^3/(\text{weight}) = \pi a^3 \rho n/6$  can be determined. Thus the two determinations permit a calculation of  $n$  and  $a$  separately. On allowing the suspension to settle, the larger particles fall more rapidly, and by measuring the transmission at various time intervals it is possible to determine the numbers of particles of various sizes, i.e., the size distribution.

Such measurements of particle size for a number of minerals have been made by Haywood (Proc. Inst. Mech. Eng. 1938, 257), and for cements by Wagner (Proc. Amer. Soc. Test. Mat. 1933, 33, 553). (See also papers by Richardson, J. Sci. Instr. 1936, 13, 229; Proc. Physical. Soc. 1943, 55, 48; Sharratt, Van Semeren, and Rollason, J.S.C.I. 1945, 64, 73.)

**Miscellaneous Applications.**—Photographic methods of photometry normally depend on comparing or measuring the light transmitted by different parts of an exposed plate. This is strictly a turbidimetric measurement, but photographic densitometry is really a subject of its own and cannot be adequately discussed in the limits of this article. It may be mentioned, however, that in the case of weak exposure of a plate such that the density after development is too small to serve as a useful measure of light intensity, an appreciable amount of light is scattered by the plate, and measurement of scattered light by nephelometric means can serve as a means of measuring the intensity of

light used to expose the plate. It has been shown (Brentano, Baxter, and Cotton, Phil. Mag. 1934, [viii], 17, 370) that for suitable conditions of plate blackening and of nephelometric set-up the scattered light is proportional to the exposure.

Other applications are to solutions of sugar, syrup, beer, etc., where measurements are made from consideration of appearance rather than actual determination of suspended impurities.

#### BIBLIOGRAPHY.

In addition to the various papers mentioned already, reference may be made to a comprehensive paper by Wells (Chem. Rev. 1927, 3, 331), which discusses fully the theory of nephelometric and turbidimetric measurements. There is a very useful textbook (J. H. Yoe and H. Kleinmann, "Photometric Chemical Analysis," Vol. II, "Nephelometry," Chapman and Hall, 1929), which describes a number of instruments and gives a large number of methods for estimation of materials, inorganic and organic.

G. F. L.

NEPHRITE (v. Vol. VII, 76b).

NEPOUITE (v. Vol. V, 430a).

NERADOL (v. Vol. VII, 257c).

NERAL (v. *Citral* b, Vol. III, 184a).

NEROL (v. Vol. V, 518a).

**NEROLI, ESSENTIAL OIL OF.** *Oil of Orange Flowers.* The oil distilled from the fresh flowers of bitter orange *Citrus bigaradia* Risso, Fam. Rutaceæ. Most of the oil is distilled in the South of France, particularly in the Alpes-Maritimes. Two crops are gathered in the year in May and October: Spain, Italy, Sicily, and Tunis all produce the oil in small quantities. The oil is used in the manufacture of Eau de Cologne and other perfumes. The residual aqueous distillate is sold as orange-flower water.

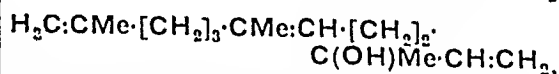
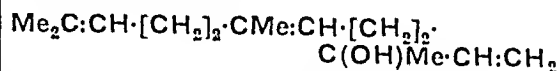
**Constituents.**—The chief aromatic constituents are acetic esters of nerol, linalol, farnesol, geraniol, and phenyl ethyl alcohol. Methyl anthranilate is the body which has the characteristic odour of neroli oil and is present to the extent of 0.4–1%. Other constituents are terpineol, decylaldehyde, jasmone, indole, phenylacetic acid, and a trace of paraffin hydrocarbons.

**Characters.**— $\rho_{15.5}^{20}$  0.870–0.895,  $[\alpha]_D^{20} +2^\circ$  to  $+6^\circ$  (occasionally higher)  $n_D^{20}$  1.468–1.477. Esters, calculated as linalyl acetate, 8–20%. The oil obtained by redistillation of orange-flower water has a higher content of methyl anthranilate (from 5 to 6 per cent.).

The oil from the fresh flowers of the sweet orange is sometimes distilled and has a similar composition.

C. T. B.

*d*-NEROLIDOL,



b.p. 125–127°/4.5 mm.,  $\rho^{15}$  0.880,  $n_D$  1.4802,  $[\alpha]_D +12.48^\circ$ , occurs in neroli oil (*Citrus bigaradia*) and in Peru balsam (v. TERPENES).

J. L. S.

NERVON (v. Vol. VII, 331d).

NESSLER'S REAGENT (*v.* Vol. II, 572c).

NEURINE (*v.* Vol. III, 94a).

**NEUTRON** (Sym.  $\frac{1}{0}n$ ). The neutron is one of the fundamental particles. It is electrically neutral and its mass, obtained from measurements on the disintegration of deuterium by  $\gamma$ -rays (Chadwick, Feather, and Bretscher, *Proc. Roy. Soc.* 1937, A, 163, 366) is  $1.00894 \pm 0.00002$  mass units (scale  $^{16}\text{O} = 16.00000$ ). This is  $0.00081$  mass unit greater than the mass of the hydrogen atom, and therefore the free neutron is expected to be unstable, transforming into a proton and an electron, with a "half-life" of a few hours. The neutron spin is a half-integral multiple of  $\hbar/2\pi$  and, like that of the proton and the electron, is probably equal to  $\frac{1}{2}(\hbar/2\pi)$ . As would be expected from its half-integral spin, the neutron obeys Fermi-Dirac statistics (*i.e.*, the Pauli exclusion principle holds for neutrons) (Bethe and Bacher, *Rev. Mod. Physics*, 1936, 8, 89). The neutron magnetic moment has been directly determined (Alvarez and Bloch, *Physical Rev.* 1940, [ii], 57, 111) to be  $-1.93 \pm 0.02$  nuclear magnetons.

**Discovery.**—The existence of a "neutron" had been predicted many times before its discovery, one of the most accurate and definite statements on its expected properties being made by Rutherford (*Proc. Roy. Soc.* 1920, A, 97, 396). The discovery arose from studies in the artificial disintegration of light nuclei, using the high-energy  $\alpha$ -particles emitted by some of the naturally occurring radioactive elements (radium, polonium, etc.). Bothe and Becker (*Z. Physik*, 1930, 66, 289) found that beryllium, when bombarded with high-energy  $\alpha$ -particles, emitted a penetrating radiation which they considered to be a very energetic  $\gamma$ -ray. Curie and Joliot (*Compt. rend.* 1931, 193, 1412, 1415) noticed that this radiation ejected protons from paraffin wax, and concluded that, if a  $\gamma$ -ray, its energy must be of the order of 50 me.v. (fifty million electron-volts). Finally, by studying collisions between the beryllium radiation and nuclei of various masses, Chadwick (*Nature*, 1932, 129, 312) proved that it consisted of heavy neutral particles of mass approximately equal to that of the proton.

**The Neutron as a Structural Unit of the Nucleus.**—The nucleus of an atom of atomic weight  $A$  and atomic number  $Z$  contains  $Z$  protons and  $(A-Z)$  neutrons. Strong attractive forces must exist between these particles in order to overcome the electrostatic repulsion between the protons. These forces show saturation properties, that is a nuclear particle interacts with only a limited number of other particles in the nucleus, and this suggests a similarity to the valency bonds between atoms. By analogy with the homopolar bond, nuclear forces are considered to be caused by the exchange of light particles between the heavy nuclear particles. These light particles should have a mass intermediate between the masses of the electron and proton, and may be similar to the mesons of cosmic rays (*see* Bethe and Bacher, *Rev. Mod. Physics*, 1936, 8, 83; Peierls, *Ann. Rep. Progr. Physics*, 1939, 6, 78).

**Interaction of Neutrons with Matter.**—The forces between neutrons and electrons are

very small, and therefore neutrons lose little energy when passing through the extra-nuclear structure of atoms. It is mainly by collisions with nuclei that neutrons are scattered or absorbed, and therefore lose energy. Because of the small "size" of the atomic nucleus ( $10^{-12}$  cm., *cf.* atomic dimensions,  $10^{-8}$  cm.), a neutron will, in general, traverse relatively large thicknesses of matter before making a collision, when, being uncharged, it can easily penetrate into the nucleus to form a "compound" nucleus (Bohr, *Nature*, 1936, 137, 344). The binding energy of a neutron in an average nucleus is of the order of 8 me.v.; this energy, plus the kinetic energy of the incident neutron, will be available for the general excitation of the compound nucleus, which is therefore in a highly excited state, at least 8 me.v. above the ground state. A short time after its formation, the excited compound nucleus either reverts to the ground state by the emission of  $\gamma$ -ray quanta or disintegrates by emission of heavy particles. In discussing these processes it is convenient to divide neutrons into two classes, slow and fast, with a dividing line at approximately 1,000 e.v.

**Fast Neutrons.**—For incident neutrons of energies up to 5 me.v. the most probable modes of de-excitation of the compound nucleus are by emission of a neutron of lower energy (the inelastic scattering process) or, in light elements, by emission of a proton or an  $\alpha$ -particle. For neutrons of higher energies, more than one neutron can be emitted, and charged particle emission can take place in heavier nuclei. A rare alternative mode of de-excitation for all fast-neutron energies is by  $\gamma$ -rays, and an alternative in heavy elements (thorium, protactinium, uranium, neptunium (?), plutonium) is fission.

The quantum levels of the compound state formed by capture of a fast neutron form a continuum. Therefore the probability of capture in this energy region, as a function of neutron energy, shows no pronounced maxima or minima; but if charged particles are emitted, a number of discrete energies only may appear, due to resonance penetration of the potential barrier opposing their exit. The cross-sections for fast-neutron processes, all of which may lead to radioactive products, are of the order of  $10^{-24}$  sq. cm.; that is, the mean free path of a fast neutron in a solid is approximately 10 cm.

Another type of fast-neutron process of the same order of importance, but not involving a compound nucleus, is that of elastic scattering. In this process kinetic energy and momentum are conserved, so that marked loss of neutron energy results only from collision with light nuclei.

**Slow Neutrons.**—By passing fast neutrons into a medium containing light nuclei, it is possible to slow down the neutrons to energies as low as  $1/40$  e.v. If the light nuclei do not capture these low-energy neutrons a "gas" of slow neutrons is produced, in thermal equilibrium with the nuclei of the medium. Heavy water and graphite are media which, most completely, produce this effect; ordinary water and paraffin wax are often used as slowing-down media, but the protons capture neutrons to a

certain extent so that complete "thermal equilibrium" cannot be attained.

Capture of these slow neutrons by nuclei now leads to a compound state the excitation energy of which is about 8 me.v. (the neutron binding energy) plus, at most, a few electron volts (the kinetic energy). In this excitation-energy region the quantum levels of the compound nucleus are sharp and distinct [1/10 to a few electron volts wide, and separated by about 100 e.v. in medium and heavy nuclei (Bohr, *l.c.*)]. The probability of capture of slow neutrons shows, therefore, strong maxima when the neutron energy plus the binding energy corresponds to a quantum level of the compound nucleus. In addition, because of the large de Broglie wave-length of slow neutrons, the captive cross-sections are much greater than those of fast neutrons and can be as much as  $10,000 \times 10^{-24}$  sq. cm.; that is, the mean free paths are of the order of 0.01 mm. [*E.g.*, the captive cross-sections for absorption of thermal ( $\sim 1/40$  e.v.) neutrons are  $3,000 \times 10^{-24}$  sq. cm. for cadmium and  $30,000 \times 10^{-24}$  sq. cm. for gadolinium.]

De-excitation from these levels almost invariably takes place by  $\gamma$ -ray emission. Lithium and beryllium, however, emit  $\alpha$ -particles, and nitrogen emits protons, following capture of slow neutrons, and fission occurs in  $^{235}_{92}\text{U}$  and  $^{239}_{94}\text{Pu}$ . This property of  $^{235}_{92}\text{U}$  (i.e., that it is capable of fission by slow neutrons) has enabled chain reactions to be established in mixtures of uranium and graphite or heavy water.

**Production of Neutrons.**—One of the most convenient sources of neutrons is beryllium undergoing bombardment by  $\alpha$ -particles or by  $\gamma$ -rays.  $\alpha$ -Particle bombardment is usually carried out by intimately mixing a radium salt with beryllium, and  $\gamma$ -ray bombardment by surrounding radium with a block of beryllium. The successful development of methods of accelerating charged particles to high energies (high-voltage machines, cyclotrons, etc.) has led to the production of neutron sources of high intensity and having other desirable properties. The bombardment of a deuterium target by deuterons yields mono-energetic neutrons. High-energy deuteron bombardment of beryllium gives a very intense neutron source, and from deuteron bombardment of lithium in a medium-sized cyclotron, neutrons with energies up to 25 me.v. can be obtained. (For details of these and other reactions, see Livingston and Bethe, *Rev. Mod. Physics*, 1937, 9, 290).

The fission of uranium is accompanied by the emission of two or three neutrons per nucleus (see, for example, von Halban, jun., Joliot, and Kowarski, *Nature*, 1939, 143, 470, 680). These neutrons are captured by uranium or other nuclei or escape through the sides of the block of material used. However, in a reacting pile the equilibrium neutron-density can be several orders of magnitude greater than that which can be obtained by other means (see Smyth, *Rev. Mod. Physics*, 1945, 17, 351).

**Detection of Neutrons.**—The most convenient way of making measurements on fast neutrons is to use a hydrogen-filled detector (cloud chamber, ionisation chamber, etc.). The neutrons transfer a part, or all, of their energy

to the hydrogen nuclei, and the energies and number of the recoil protons can be related to the neutrons producing them. The efficiency for fast-neutron detection in the usual type of instrument is low—of the order of  $10^{-3}$ . Slow-neutron measurements are usually made with ionisation chambers containing boron or lithium, which emit  $\alpha$ -particles after capturing a slow neutron; the efficiency of detection of slow neutrons can be made unity. Alternatively, the radioactivity induced in an element is often used for slow-neutron, and occasionally for fast-neutron detection. Manganese and dysprosium are common slow-neutron indicators.

**Practical Applications of Neutrons.**—The ease with which neutrons penetrate into the nuclear structure makes them the most important particles with which to investigate this structure. The high neutron-intensities in a uranium pile will make possible the production of very large amounts (thousands of curies) of artificially radioactive substances, of great importance as tracers in physical, chemical, and biological studies. These artificial radioactivities will also be of great value, and replace radium, in radio-therapy. It may be, also, that irradiation of tissues by fast neutrons will prove useful in the treatment of cancer (see next section).

**Biological Effects of Neutrons.**—The biological effects of fast neutrons are mostly due to the ionisation produced in living tissue by recoil protons, which have been given energy by collision with the fast neutrons. The effects are similar in quality to those due to X- or  $\gamma$ -rays, but are several times more powerful, if referred to equal numbers of ions created per unit volume of tissue. The enhanced action is thought to be due to the high density of the ions in the proton tracks as compared with the lower density in the electron tracks due to X- or  $\gamma$ -ray irradiation. The action of slow neutrons is much less than that of fast neutrons, and is largely due to  $\gamma$ -rays emitted following their capture by the atomic nuclei of living tissue. Attempts have been made, with inconclusive results, to improve cancer therapy by using fast neutrons from a cyclotron instead of X- or  $\gamma$ -rays (see Spear, *J. Sci. Instr.* 1945, 22, 21; for a general account, see D. E. Lea, "Actions of Radiations on Living Cells," Cambridge Univ. Press, 1946).

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J. D.

"NEW FORTEX" (*v. Vol. IV*, 487b).

NEWTON'S ALLOY (*v. Vol. VII*, 241d).

N'GART OIL (*v. Vol. IV*, 86c).

**NICCOLITE.** Nickel arsenide,  $\text{NiAs}$ . Small amounts of iron, cobalt, and sulphur are often present, and by increasing replacement of arsenic by antimony the mineral grades into breithauptite ( $\text{NiSb}$ ). Niccolite crystallises in



the hexagonal system, but crystals are rare, and the mineral is usually massive, reniform, with a columnar or reticulated structure. It has a distinctive pale copper-red colour with metallic lustre (hence called *Kupfernickel*, copper-nickel), and brownish-black streak. By its greater hardness ( $5-5\frac{1}{2}$ ), and brittleness it is readily distinguished from native copper.  $\rho$  7.78. Niccolite emits arsenical fumes of garlic-like odour when heated on charcoal, and gives the nickel test with dimethylglyoxime. The mineral is often coated with a pale-green decomposition film of annabergite (nickel bloom),  $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ .

Niccolite is a minor source of nickel, notably in the copper-bearing shales of Mansfeld in Germany, and in the nickeliferous pyrrhotite ores of Sudbury, Ontario; it is also frequently present in vein deposits containing cobalt and silver minerals.

D. W.

**NICKEL.** Sym. Ni. At. wt. 58.69. At. no. 28. Isotopes 58, 60, 61, 62, 64.

Although the Chinese have used a nickel-copper-zinc alloy for over 2,000 years, nickel was not discovered until 1751, when Cronstedt found the element in *niccolite*, obtained from a Swedish cobalt mine. Bergman isolated the metal and produced the first pure nickel in 1775. The properties of nickel were described by Richter in 1805.

#### MINING, SMELTING AND REFINING.

**Distribution of Ores.**—Ores containing nickel occur in many parts of the world and numerous deposits, chiefly low-grade, were worked in the nineteenth century. World production in 1870 was about 500 tons, mostly obtained from Norway. Germany, Scandinavia, Austria, and Pennsylvania produced smaller quantities. Russian nickel-mining dates from 1866 and small, low-grade deposits in the Urals have been worked intermittently since then, but the output has always been small. Ores from New Caledonia were exported to Europe in 1875 and shortly afterwards production began in Canada, where large, rich deposits had been found earlier in the century. A potentially important mine near Petsamo, Finland, was in the development stage in 1939. Low-grade ore bodies are also being developed in Brazil and Cuba to produce ferro-nickel. Mayari pig, a low nickel-bearing iron, has been obtained from Cuban properties for many years. The abundance of nickel in the 10-mile depth of the earth's crust was estimated by Wells to be 0.016% (U.S. Geological Survey, 1943).

Current world nickel output in 1939 was about 100,000 tons, Canadian production accounting for about 90% and New Caledonia for most of the balance. Norwegian and Russian production remained low. Some by-product nickel was obtained in the refining of other metals, notably copper and cobalt, but the amount was small in relation to world output.

**New Caledonia Production.**—The New Caledonia ore is a hydrated nickel magnesium silicate, *garnierite*,  $[(\text{Ni}, \text{Mg})\text{SiO}_3 \cdot \text{H}_2\text{O}]$  (v. Vol. V, 429d), which contains about 5–6% of

nickel. It is quarried from small ore-bodies which outcrop in many parts of the island. Production methods are governed by the availability of suitable fuel and fluxes. Blast-furnace treatment is employed, using gypsum (hydrated calcium sulphate) as a flux, and imported coke. The sulphate is reduced to sulphide, and the sulphur combines with the nickel to produce a nickel sulphide matte. This is bessemerised to oxidise the bulk of the sulphur, a siliceous flux is added to slag off the iron, and the resultant matte is roasted to eliminate the remaining sulphur. The oxide is then ground and mixed with farinaceous material, which acts both as a binder and a reducing agent, and the product briquetted into circular discs or cubes, known as "rondelles." These are heated for from one to two days in close contact with charcoal and, when reduction is complete, assay about 99.25% nickel.

**Canadian Production.**—The Canadian mines, which dominate the industry, occur on the periphery of an oval-shaped basin, 36 miles long and 16 miles wide, near Sudbury in Northern Ontario. Many ore bodies have been found and the chief producing mines are of vast extent, uniform in composition, and rich in other metals. The ore contains about 2% of nickel, with a varying copper content, usually about 4–5%, and substantial amounts of the "platinum group" metals, together with silver, gold, cobalt, selenium, and tellurium. Owing to the richness of the ore and the highly developed methods of treatment employed, the area is the world's lowest-cost producer.

The chief minerals in the Canadian deposits are *pyrrhotite* ( $\text{Fe}_9\text{S}_8$ ), *chalcopyrite* ( $\text{CuFeS}_2$ ) (v. Vol. II, 517c), and *penillandite*  $[(\text{Ni}, \text{Fe})_{11}\text{S}_{10}]$ . In parts the two last named are found in masses in a fairly pure state, but normally they are intermixed with the iron sulphide in a basic gangue. The separation of the copper and nickel is effected by the "Orford" process.

#### SMELTING.

Smelting procedure involves four main stages—concentration, calcination, reverberatory-furnace treatment, and bessemerising to produce a suitable matte.

The object of concentration is to remove the rock and separate as much copper as possible. This is achieved by the flotation process (v. Vol. V, 263d), in which the surface properties of finely divided particles are utilised to separate the different constituents. The separation is effected in tanks filled with a suitable liquid for the materials being treated. Rock particles, which are easily wetted, sink quickly; sulphide particles, which do not wet so quickly, tend to float for a time which can be extended by adding reagents to the slurry to enable the mineral particles to resist wetting. Air is blown through the tanks and the sulphide particles become attached to the bubbles and are carried to the surface. The addition of fine oil prevents the bubbles breaking when they reach the surface. The copper-bearing mineral floats to the top; the nickel sulphide remains at a lower level; the iron-bearing mineral is lower still and the rock falls to the bottom.



The separation of copper from nickel is rough but effective, about half the copper being recovered by flotation, and the need for a furnace separation treatment of this part is thus eliminated. The pyrrhotite contains a good deal of nickel and goes forward for further treatment.

Preparation of the ore for flotation involves *crushing and grinding to obtain a finely divided powder*. This is carried out in ball and rod mills, which feed the crushed material with water to bowl classifiers, which pass suitable material forward to the flotation tanks and return coarse material for further treatment. The tanks are divided into groups, the first producing copper-rich material and feeding the tailings to the group which produce a nickel-copper concentrate. Both the concentrates are treated again to secure a better separation. Dewatering is carried out in settling tanks, in tray thickeners, and by filtration, the residual moisture being eliminated in the calcining furnaces.

The object of calcining is to reduce the sulphur content to the point at which just enough is available to form a nickel-copper-iron sulphide matte for the next operation. The roasting is carried out in furnaces having free access to air, the sulphur being converted to sulphur dioxide, which is piped off with the other converter gases and used for the manufacture of sulphuric acid by the contact process, the acid in turn being used to produce the sodium acid sulphate which is required in the Orford nickel-refining process. The reaction is exothermic and no heat is required except for starting the furnaces. The sulphur content is reduced from 28 to 16% and the concentrate discharged to the reverberatory furnaces.

Reverberatory furnace treatment is designed to eliminate the remaining gangue, which is slagged off, and to bring the mixed sulphides to the molten state suitable for feeding to the converters. Roverslag from the converters is also treated with the sulphides for recovery of nickel and copper.

Treatment in Bessemer converters, to eliminate the iron and further reduce sulphur by oxidation, is the final stage of smelting. Enough silica is added to form an iron silicate which can be slagged off. The resultant matte contains about 80% of nickel and copper.

#### REFINING.

The first process in refining is the separation of the copper from the nickel by the "Orford" process. This involves heating the matte in a cupola with sodium acid sulphate (nitro cako) and coke, which gives a molten product containing sulphides of copper, nickel, and sodium. The copper and sodium sulphides unite in a solution which is lighter than the nickel sulphide, so that when poured into pots the product settles into two layers, the top portion being copper and sodium sulphides and the bottom portion nickel sulphide. The process is often referred to as the "tops and bottoms process." A better separation is obtained by remelting the bottoms to produce "second bottoms" which contain about 1.5% of copper and 72% of nickel.

Final refining is carried out by the electrolytic process in Canada or by the "Mond" process in

South Wales. In the former method the cobalt content, which averages about 0.5%, remains in the nickel. In the Mond process the cobalt is isolated and recovered. Both processes permit the recovery of the precious metal content of the ore. The selenium and tellurium follow the copper and are recovered in the copper refinery.

Several treatments are necessary to produce nickel in the forms required in commerce, and as a preliminary to electrolysis. The second bottoms are broken up, ground, and any remaining sodium sulphide leached out with hot water. Hot dilute sulphuric acid is used to dissolve the remaining iron. The copper is chloridised by calcining the sulphide with about 15% of coarse salt, the cuprous chloride being then dissolved out with hot water.

The product, now known as green nickel oxide, is then calcined with soda ash, and the sodium salts formed are washed out with hot water. This produces a commercial product known as black nickel oxide, which has uses in the pottery, electrical, enamelling, and fat-hardening industries. It is also used as a basis in the production of various nickel salts.

Metallic nickel is produced from the sulphides, which are reduced to oxide in a different way. Following treatment for removal of iron, the washed material is calcined with coke in Dwight-Lloyd sintering machines. In these machines the sulphides are carried on moving belts under a blast of air and flame and after one or two passes are converted to oxide. The sinter is then melted with coal and anode scrap and cast into anodes.

Purification of the impure nickel is achieved by electrolysis, the hot, nickel-bearing solution from the anode compartments being pumped over nickel powder to precipitate the copper, passed through Dorr thickeners to eliminate solids, while air is blown through to oxidise the iron, which is precipitated as ferric hydroxide. The acid set free by the hydrolysis of ferric iron is neutralised by adding a suspension of nickel carbonate in water to the solution. After filtering, the solution flows to the cathode compartments and the nickel is deposited on starting sheets, from which it is stripped and cut up to form the market product. The precious metals are recovered from the anode slimes.

#### THE MOND PROCESS.

The nickel-refining process operated in South Wales is based on work carried out in the late Dr. Ludwig Mond's laboratory in the last century, when it was discovered that if carbon monoxide is passed over freshly reduced nickel at temperatures below 80°C. a volatile metallic compound, nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , results and that this compound can be decomposed into nickel and carbon monoxide by heating to about 180°C. When it was shown that no other metal reacted in precisely the same way, the possibilities of using the reaction as a new nickel-refining process were apparent.

The process starts with ground sulphide produced by the Orford process. This is passed through ball mills to obtain a fine powder, which is calcined, the sulphur being eliminated as sulphur dioxide. The resultant oxide is then

ground and reduced to metal by water gas containing roughly 60% of hydrogen and 36% of carbon monoxide. In the reducers, which are tall, cylindrical vessels, the oxide is passed over a series of superimposed plates, the reduction temperature of approximately 350°C. being maintained by a hot-air circulating system. The water gas enters at the top and leaves at the bottom. Owing to the low temperature employed, about 97% of the reduction is due to the endothermic reaction with the hydrogen, which is from twenty to forty times as rapid as the exothermic reaction with carbon monoxide. The effluent gas, which is rich in carbon monoxide, is suitable for the formation of nickel carbonyl in the volatilisers.

The reaction in the volatilisers, to which the crude metal is transferred, is exothermic, the heat generated being dissipated by radiation and conduction. A temperature of 50–60°C. is maintained. The metal travels downwards and the carbon monoxide upwards. The concentration in the exit gas ranges from 200 g. to 25 g. of nickel per cubic metre, the higher figure being reached in the first volatiliser.

Decomposition is effected at a temperature of about 180°C. In the decomposers the nickel carbonyl is brought into contact with heated nickel pellets on which the nickel is deposited. These pellets, when built up to about 10 mm. diameter, are the final product. Close temperature control is required, as carbon monoxide is liable to break down into carbon and carbon dioxide at 200°C. The carbon monoxide released in the decomposers is returned to the reducers to form more carbonyl.

The precious metal and cobalt contents of the ore are recovered from the residues from the volatilisers.

#### THE PROPERTIES OF NICKEL.

Nickel exists in only one phase which is stable at all temperatures. It has a magnetic transformation point at about 350°C., and changes in other physical properties occur at approximately this temperature, but whether these changes are interconnected is not known, as no alteration in the structure of the metal has been observed. The properties of the metal have been determined by many investigators working with metal of different compositions, which fact, combined with the lack of uniformity in melting conditions, heat treatment, and crystal structure, appreciably affects the results obtained and makes comparisons difficult. Several methods of producing nickel of academic purity have been employed during recent years and the results of work on high-purity material have been included where available.

**Production of High-Purity Nickel.**—The usual method is to prepare high-purity nickel salts for conversion to oxide and reduction with hydrogen or by direct electrolysis of the salts. Melting pure nickel in hydrogen or in vacuum involves the risk of contamination from the crucible. Electrolysis, even in a chloride bath, leaves traces of sulphur. The product of the carbonyl process tends to be contaminated by carbon and oxygen. The most satisfactory method, according to Wise

and Schaefer (*Met. and Alloys*, 1942, 16, 424), is by electrodeposition from a very pure nickel chloride electrolyte, using insoluble iridium-platinum anodes. This method has yielded a product containing 99.99% of nickel and Cu 0.0008, Fe 0.0005, Co 0.0003, and C 0.0025%.

**Influence of Impurities on Nickel.**—The effect of impurities on the malleability of nickel was investigated by Merica and Waltenberg (*J. Res. Nat. Bur. Stand.* 1925, 19, 155) who found that when nickel is melted in the presence of oxygen the oxide formed (NiO) forms a eutectic with nickel. The solubility of oxygen in molten nickel, over a range of temperatures, was determined by Hensel and Scott (*Trans. Amer. Inst. Min. Met. Eng.* 1933, 104, 139) using vacuum fusion in an induction furnace. Absorption increased with temperature as shown by the following results: 1,465°C., 0.294%; 1,550°C., 0.423%; 1,650°C., 0.526%. The nickel-oxygen diagram showed a eutectic at 0.214% oxygen at 1,435°C. Turbulence and time increased the rate of absorption. Merica and Waltenberg found nickel containing nickel oxide, at least up to the eutectic composition, to be malleable. Nickel melted under hydrogen or under carbon monoxide also proved to be malleable. Their experiments showed that carbon monoxide, carbon dioxide, oxygen, and nitrogen in normal amounts did not render nickel non-malleable, but that sulphur had a profoundly adverse effect. They placed the permissible limit for sulphur in cast nickel below 0.005%. Electrolytic nickel containing less than 0.005% was malleable without special treatment. As little as 0.01% of sulphur added to remelted electrolytic nickel rendered it almost completely non-malleable. They attributed the effect of sulphur to the formation of a eutectic film of nickel and nickel sulphide (Ni<sub>3</sub>S<sub>2</sub>) on each metallic grain of nickel, which lowered the intercrystalline cohesion of the mass of grains even at low temperatures. This eutectic melted at 630°C., and at higher temperatures there was practically no cohesion between the nickel grains. The addition of 0.5–1.0% of manganese to nickel containing more than 0.01% of sulphur improves malleability. Manganese combines with nickel sulphide to form manganese sulphide and nickel, the two forming a eutectic melting at 1,325°C. Distribution is in the form of small globules along the grain boundaries. The addition of 0.05–0.10% of magnesium completely restores malleability. Magnesium sulphide is insoluble in molten nickel and is found dispersed throughout the grains. Magnesium is also used as a degasifier.

Hydrogen is readily soluble in nickel. When the metal is heated or in the molten state, the gas is occluded. The precise form in which the hydrogen exists has not been determined, but Hüttig (*Z. angew. Chem.* 1926, 39, 67) has suggested that the gas forms a compound with nickel and that the balance is in the form of a solid solution, the relative amounts of each varying with temperature. The solubility of hydrogen in nickel was determined by Sieverts (*Z. Metallk.* 1929, 21, 37), but his figures have been disputed. As with other gases in metals, the solubility of hydrogen at a constant tempera-

ture is proportional to the square root of the pressure. The adsorption of hydrogen by nickel has been investigated by many workers. Taylor and Burns (*J. Amer. Chem. Soc.* 1921, 43, 1273) found that nickel reduced at 600–700°C. adsorbed comparatively little hydrogen, an interesting point as nickel reduced at this temperature is inert as a catalyst. Huntzicker and Kahlenberg (*Trans. Electrochem. Soc.* 1933, 63, 349) investigated the relationship of hydrogen to specially prepared pure nickel, and concluded that nickel was normally a passive metal, but that the presence of hydrogen raised its activity so that it replaces copper, silver, and other metals from solutions.

No figures are available on the solubility of nitrogen in nickel, but Lombard (*Rev. Mét.* 1929, 26, 343) investigated the diffusion of nitrogen through nickel and found it to be very low, indicating a low solubility in the solid state.

The presence of nitrogen in gas extracted from nickel has been reported.

**Crystal Structure and Lattice Dimensions.**—Nickel crystallises in face-centred cubes. The side of the unit cube was found by Kennedy (*J. Res. Nat. Bur. Stand.* 1930, 5, 1300) to be 3.525 Å. This figure for the lattice dimension gives a calculated density of 8.917 g. per c.c.: experimentally determined values of 8.907 for cast and 8.901 for worked material were obtained from the same material. The maximum density was obtained in coarsely crystallised ingot metal. Owen and Yates (*Phil. Mag.* 1936, [vii], 21, 809) obtained a figure of 3.51645 Å. at 0°C. by X-ray measurements. They confirmed that the structure remained face-centred over the range investigated, 0–600°C.

**Melting-Point and Latent Heat of Fusion.**—Wensel and Rocser (*J. Res. Nat. Bur. Stand.* 1930, 5, 1300), using the optical pyro-

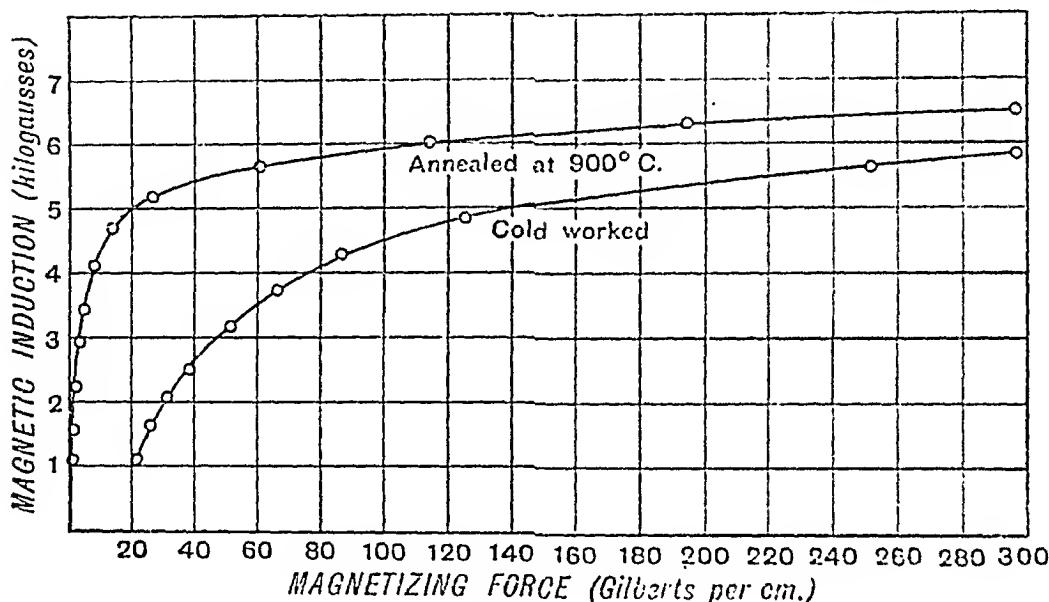


FIG. 1.

meter method, found the melting- or freezing-point of high-purity nickel to be 1,455°C. They checked this value with many determinations. The generally accepted melting-range for commercial nickel is 1,435–1,445°C.

White (*Chem. Met. Eng.* 1921, 25, 17) determined the latent heat of fusion of a nickel melting at 1,450°C. to be 73 g.-cal. per g.

**Specific Heat.**—Sykes and Wilkinson (*Proc. Physical Soc.* 1938, 50, 834) give the following values (in g.-cal. per g. per °C.) for specific heat, being the average for samples of vacuum-melted and of sintered carbonyl nickel of high purity: 100°C., 0.1123; 200°C., 0.1225; 300°C., 0.1367; 400°C., 0.1267; 500°C., 0.1265; 600°C., 0.1326. White (*Chem. and Met. Eng.*, 1921, 25, 17) states that the mean specific heat between 20°C. and the melting-point is 0.134 g.-cal. per g. per °C. Values obtained by earlier investigators are given by Stoner (*Phil. Mag.* 1936, [vii], 22, 81) in a review of the factors involved in determining the specific heat of nickel.

**Appearance and Colour.**—Nickel has a

lustrous, silver-white colour with a slight, steel-grey tinge. The metal is sufficiently hard to take a mirror polish.

**Density.**—The density of nickel is 8.90 g. per c.c. Peffer (*J. Res. Nat. Bur. Stand.* 1930, 5, 1299), using high-purity nickel, prepared by Jordan and Swanger, obtained a value of 8.907 g. per c.c. at 23°C. for ingot metal, and 8.901 g. per c.c. at 25°C. for rolled material annealed at 950°C.

**Electrical Resistivity and Temperature Coefficient.**—Wenner and Caldwell (*J. Res. Nat. Bur. Stand.* 1930, 5, 1301) found the electrical resistivity of high-purity nickel to be 7.236 and 7.290 microhms per cm. cube at 20°C. for annealed and cold-drawn material, respectively. The temperature coefficient of the resistivity of the metal per °C. between 0° and 100°C. was 0.00667. Wise and Schaeffer (*Met. and Alloys*, 1942, 16, 424) give values of 6.141 (0°C.) and 6.844 microhms per cm. cube (20°C.), the figures being based on determinations by Umbreit on high-purity electrolytic nickel.

The temperature coefficient was 0.00682. The electrical resistivity of commercial nickel is generally higher, and is usually in the range of 9–10.5 microhms per cm. cube.

**Magnetic Properties.**—Nickel is ferromagnetic below, and paramagnetic above, the magnetic transformation point. The Curie point depends somewhat on previous history. Sanford (J. Res. Nat. Bw. Stand. 1930, 5, 1302) made several determinations by the magnetometric method, using an astatic magnetometer and gave an average value of 380°C. on heating and 371°C. on cooling from approximately 500°C. Kussmann and Schultz (Physikal. Z. 1937, 38, 42) studied the question of the Curie point and its relation to the change point in the temperature-electrical resistance curve. They concluded that one property cannot be deduced from the other and that the Curie point in a perfectly homogeneous material is an absolute

in Fig. 2. The maximum permeabilities obtained were:

(111)	. . . . .	3,090
(110)	. . . . .	2,100
(100)	. . . . .	1,820

**Hysteresis:**

	$H_c$	$B_r$
(100)	. . . . . 0.8	1,500
(110)	. . . . . 0.6	1,800
(111)	. . . . . 0.5	1,200

The magnetic induction of polycrystalline high-purity nickel as determined by Yensen (*ibid.* 1942, 16, 427) is shown in Fig. 3, with a portion of an hysteresis loop from  $B$  5,000. The coercive force ( $H_c$ ), from  $B=5,000$  gauss, was found to be 2.73 oersteds per cm.

The ferromagnetic change in length per unit length for nickel of 99.98% purity was found

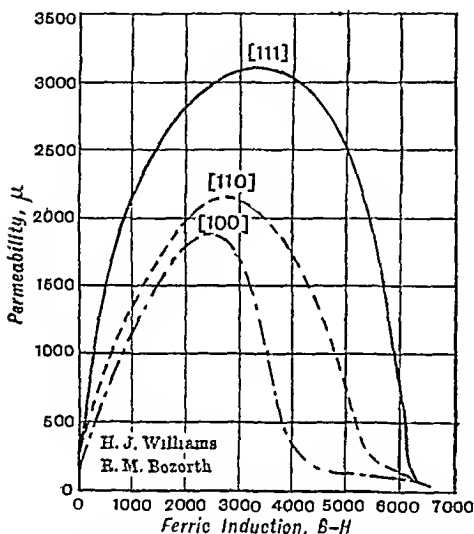


FIG. 2.—PERMEABILITY VALUES FOR HIGH-PURITY (SINGLE-CRYSTAL) NICKEL.

point and not a range. The mean value obtained by these investigators was approximately 353°C. Earlier workers obtained values varying from 330° to 368°.

Sanford investigated the magnetic properties of high-purity nickel both as cold-worked and after annealing. The effect of annealing on the normal induction is shown in Fig. 1. His value for the saturation value of intrinsic induction ( $B-H$ ) $_{\infty}$  was 6,150 gauss; this figure was obtained by earlier workers. Bozorth and Williams (Met. and Alloys, 1942, 16, 427) give a figure of 6,500 gauss, which was estimated from results obtained in examining the magnetic properties of single-crystal nickel made by melting very fine nickel powder in pure hydrogen. The saturation value is a function of the constitution and is not otherwise dependent upon its condition.

Bozorth and Williams (*l.c.*) also examined the magnetic induction and permeability of the same nickel. The permeability values are given

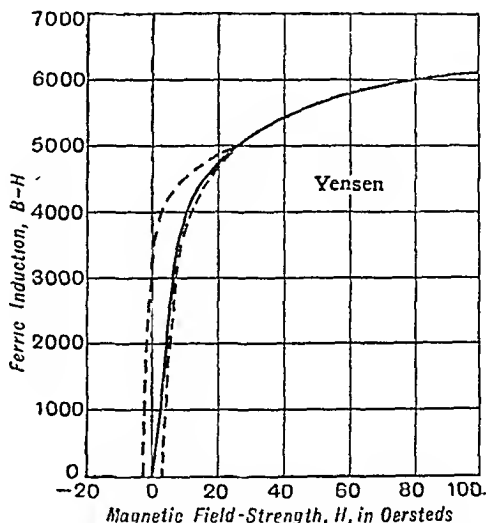


FIG. 3.—MAGNETIC INDUCTION OF VERY PURE POLYCRYSTALLINE NICKEL.

by Owen and Yates (Phil. Mag. 1936, [vii], 21, 809) to be about  $2.4 \times 10^{-4}$ , which is much higher than the values previously recorded for nickel of lower purity.

**Thermal Expansion.**—Owen and Yates measured the thermal expansion of 99.98% pure nickel by X-ray measurements at 0–600°C. The lattice parameter was measured, and it was found that up to 370°C. the lattice expanded gradually at first but rapidly between 310° and 370°C., until at the latter temperature it had an abnormally high coefficient of expansion, but there was no evidence of thermal hysteresis. Above 370°C. the coefficient of expansion rapidly decreased, falling to quite a low value before assuming at 420°C. a value which increased up to the highest temperature at which the measurements were made. The results are given in Table I.

Adensted (Ann. Physik, 1936, 26, 69) reported on the thermal expansion of nickel (99.8% purity) at low temperatures (0° to –195°C.).

TABLE I.—THERMAL COEFFICIENT OF EXPANSION OF NICKEL.

Temperature, °C.	Lattice parameter, Å.	Thermal coefficient of expansion, $\times 10^{-6}$ .
0	3.51645	13.5
100	3.52125	14.6
200	3.52637	15.8
300	3.53177	16.6
350	3.53477	23.0
360	3.53575	25.8
370	3.53664	26.0
380	3.53730	17.5
390	3.53786	15.0
400	3.53842	15.6
500	3.54462	17.6
600	3.55087	17.8

His measurements showed good agreement with those obtained much earlier by Grüneisen (*ibid.* 1918, 55, 371). The average coefficient for the range 0° to -180°C. is  $10.22 \times 10^{-6}$ .

Hidnert (J. Res. Nat. Bur. Stand. 1930, 5, 1301) measured expansion on high-purity nickel

from 25° to 900°C., and attempted to locate a transformation region between 300° and 400°C. An irregularity in the rate of expansion at 350°C. was noted.

**Thermal Conductivity.**—Van Dusen and Shelton (*ibid.* 1934, 12, 429) measured the thermal conductivity of commercial nickel and nickel of 99.94% purity; their results are given in Table II.

TABLE II.—THERMAL CONDUCTIVITY OF NICKEL IN C.G.S. UNITS.

°C.	Commercial nickel.	High-purity nickel.
100	0.155	0.198
200	0.143	0.175
300	0.131	0.162
400	0.125	0.142
500	0.130	0.148
600	0.136	—

**Thermoelectromotive Force.**—The thermoelectromotive force of high-purity nickel against platinum was measured by Caldwell

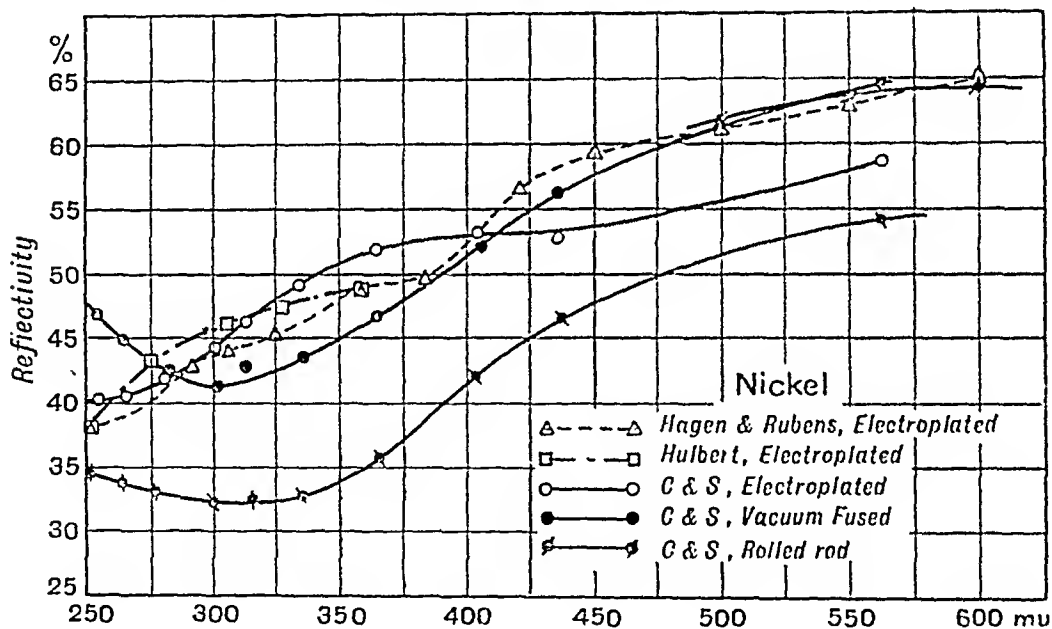


FIG. 4.

(*ibid.* 1930, 5, 1304). Nickel is thermoelectrically negative to platinum. From the figures given in Table III, it will be noted that there is a

TABLE III.—THERMAL ELECTROMOTIVE FORCE OF NICKEL AGAINST PLATINUM.

Temperature of hot junction, °C.	E.m.f. Pt-Ni, millivolts.	Temperature of hot junction, °C.	E.m.f. Pt-Ni, millivolts.
100	1.485	700	8.105
200	3.105	800	9.350
300	4.590	900	10.695
400	5.450	1,000	12.130
500	6.165	1,100	13.625
600	7.040		

change in the region of the magnetic transformation point. The values were taken with the cold junctions at 0°C.

**Electron Emission.**—The electron emission from nickel has been investigated by Benjamin (Phil. Mag. 1935, [vii], 20, 7). For wireless valve cathodes, ordinary commercial nickel, which contains traces of the activating elements magnesium and silicon, is widely used. Oxide-coated cathodes of high-purity nickel (99.99%) give only 30-80% of the emission normally obtained from the commercial product. Benjamin tested the behaviour of a series of low-alloy-content nickel cores. The initial omissions he obtained are given in Table IV.

The purity of the nickel is given as probably 99.32%.

TABLE IV.—ELECTRON EMISSION FROM OXIDE-COATED NICKEL WIRE.

Composition.	Average emission at 1,020°K. (747°c.) in milliamp. (40 v. on the plate).
Nickel . . . . .	31
Ni+0.07% Mg . . . . .	45
Ni+0.1% Ti, 0.37% Fe . . . . .	45
Ni+0.39% Ti, 1.1% Fe . . . . .	46 (from curve)
Ni+2.0% Al . . . . .	50
Ni+0.34% Mn . . . . .	20
Ni+2.33% Fe . . . . .	22.5

Thermal Reflectivity, Emissivity, and Diffusivity.—The thermal reflectivity of nickel is high and the thermal emissivity is low. Reflectivities of nickel for radiation of long wave-lengths (infra red) are 0.835 at 2 $\mu$ . and 0.870 at 3 $\mu$ . Barnes (Physical Rev. 1929, [ii], 34, 1026) gives the figure for the total emissivity as 0.19 at 1,000°c. Frazier (*ibid.* 1932, [ii], 40,

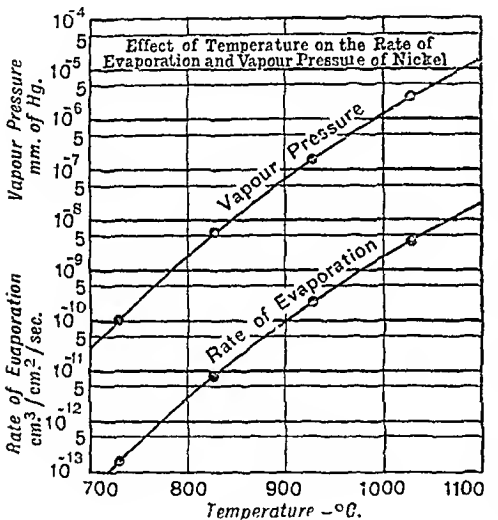


FIG. 5.

592) has reported on the thermal diffusivity of nickel of 99.25% purity, and obtained the value  $K=0.1500$ . Starr (Rev. Sci. Instr. 1937, 8, 61) measured the thermal diffusivity of high-purity nickel (99.98%) and found the value at 25°c. to be  $K=0.15885 \pm 0.0100009$  sq. cm. per sec. Optical Properties.—Polished nickel reflects a high percentage of incident light; many uses of electrodeposited coatings, notably lamp reflectors, are based on this property. Meyer (Ann. Physik, 1910, 31, 1017) found the optical constants for  $\lambda=0.589\mu$ . to be: reflectivity 65.5%; absorption index ( $K$ ) 3.42%; refractive index 1.58%. Coblenz and Stair (J. Res. Nat. Bur. Stand. 1930, 5, 1300) measured the ultra-violet reflectivity of high-purity nickel; their results are compared with the reflectivity of electro-plated nickel and commercial nickel in Fig. 4. Hlucka (Z. Physik., 1935, 96, 230) measured the reflectivity of nickel in the spectral region, and Geoghegan (Brit. J. Phot. 1934, 23, Suppl.

45) compared the reflectivity of nickel with magnesium oxide and electro-silver and obtained values of 35.48 and 63.10, respectively. Vapour Pressure.—The vapour pressure of nickel has been determined by Jones, Langmuir, and Mackay (Physical Rev. 1927, [ii], 30, 201). Their results are shown in Fig. 5. Velocity of Sound.—The velocity of sound in sheet nickel was measured by Wood and Smith (Proc. Physical Soc. 1935, 47, 149) and found to be  $5.71 \times 10^3$  cm. per second.

THE MECHANICAL PROPERTIES OF PURE NICKEL.

Very little information is available on the mechanical properties of high-purity nickel, most work having been carried out on commercial-grade material. Average tensile values of the latter are given in Table V.

TABLE V.—TENSILE PROPERTIES.

Condition.	Yield strength, tons per sq. in.		Maximum stress, tons per sq. in.	Elongation, %.	Reduction of area, %.
	0.1% permanent set.	0.2% permanent set.			
Hot rolled.	10.3	10.7	31.7	44.5	62.9
Cold drawn 24% reduction, stress relieved 300°c., 3 hours.	27.1	27.7	38.7	33.0	72.0
Cold drawn, annealed 790°c., 3 hours.	10.9	11.9	32.7	46.0	79.4

Tensile Strength and Elongation.—Jordan and Swanger (J. Res. Nat. Bur. Stand. 1930, 5, 1291) found the tensile strength of high-purity nickel to be 32.9 kg. per sq. mm. Determination of the elongation was not possible because the surface of the bar was roughened by the tension loading and the gauge marks obliterated. The investigators stated that the elongation was certainly 25% in 2 in. and probably considerably more. Ransley and Smithells (J. Inst. Metals, 1932, 2, 287) have examined the properties of nickel wire of varying degrees of purity. The effect of minor constituents on the tensile strength and elongation of 0.0425 mm. diameter wire after annealing at various temperatures is shown in Fig. 6. It will be seen that the values for pure nickel (99.91% including cobalt) fall with low-temperature annealing, while the other compositions show a slight increase in tensile strength when annealed below 400°c. Values for the recrystallisation temperature are given in Table VI. The effect of minor constituents on the tensile strength up to 1,000°c. of the same wires is shown in Fig. 7. It will be noted that all the wires have a well-defined arrest over the range 300–450°c., except the high-purity nickel, in which there is scarcely any indication of a break.

TABLE VI.—RECRYSTALLISATION TEMPERATURES.

Material.	°c.
Pure nickel (99.91%, including cobalt) . .	480
Nickel + Iron (2.33%) . . . . .	580
Nickel + Manganese (0.34%) . . . . .	620
Nickel + Magnesium (0.07%) . . . . .	640
Commercial nickel (99.39%, including cobalt)	640

Hardness.—Jordan and Swanger (J. Res. Nat. Bur. Stand. 1930, 5, 1291) measured the hardness of their high-purity nickel and obtained the following values: scleroscope 5.0; Rockwell, 100 kg.,  $\frac{1}{8}$ -in. ball, 42–44.

Fetz (Trans. Amer. Soc. Met. 1937, 25, 1030) investigated the point of recovery of cold-worked nickel at elevated temperatures. Ho

found the turning point of the hardness-recovery curve of high-purity nickel (99.99%), 80% cold-rolled, at 463°C. (30 minutes anneal). Electrolytic nickel (99.866%) as deposited recovered from an 80% reduction at 440°C. For recrystallised material the turning point was 454°C. The turning points of the hardness-recovery curves of cold-rolled nickel were found to be directly proportional to the amount of cold work. Increasing the reduction by 10% lowered the softening temperature by 23.3%.

In cold-rolled electrolytic nickel the Debye lines become completely sharp on annealing before the hardness recovers from cold work. The increase of strain-hardening during cold-rolling is not a linear function of the amount of cold work. A slight increase of hardness takes place before the release of strain-hardening. This maximum hardness has nothing to do with

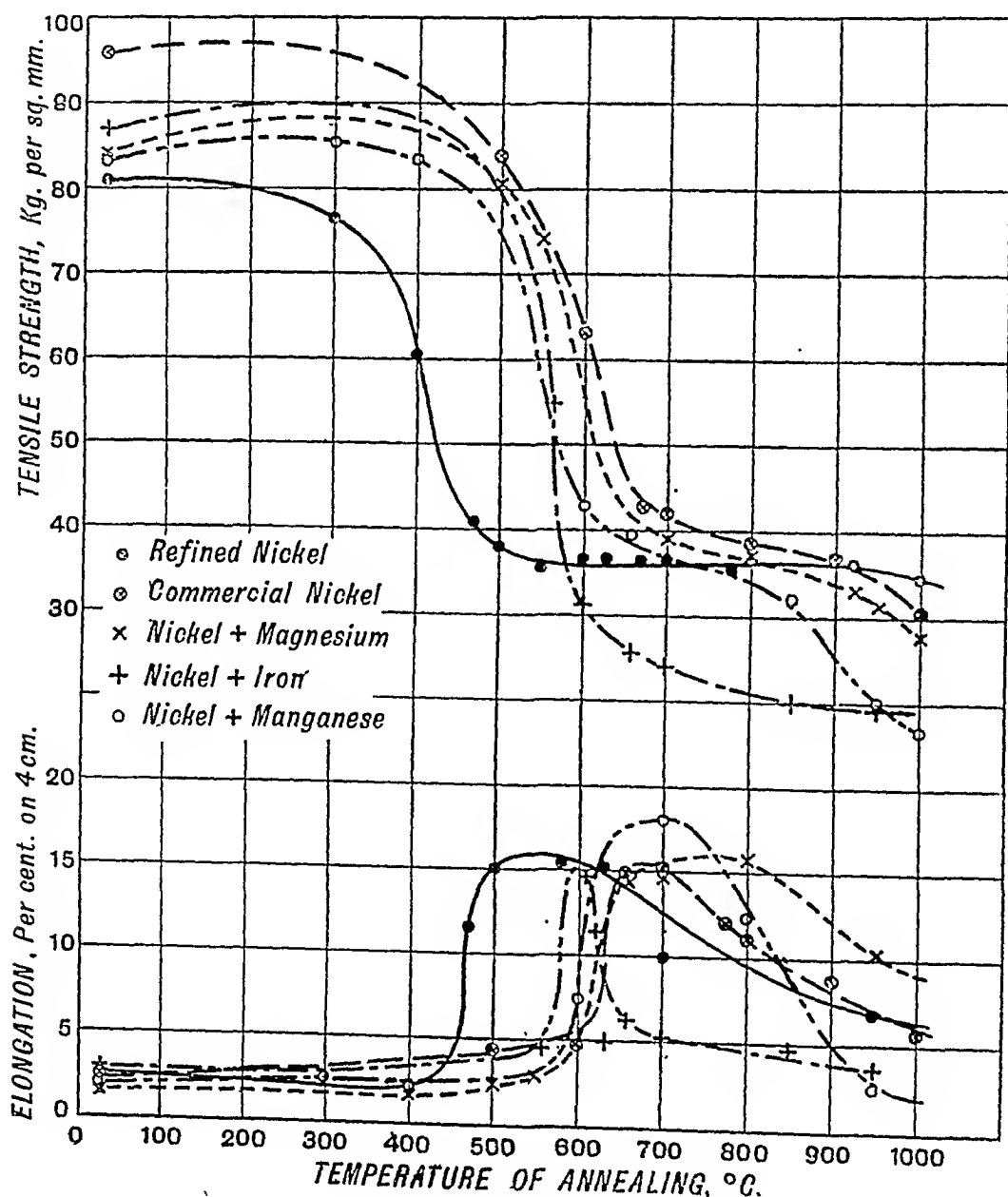


FIG. 6.



the slight rearrangement of atoms preceding the magnetic transformation.

The rate of strain-hardening of recrystallised electrolytic nickel during cold-rolling is shown in Fig. 8. The softening of the same nickel in relation to reduction is shown in Fig. 9.

The effect of other elements present upon the recovery of highly pure nickel was studied by Retz in a subsequent paper (*ibid.* 1938, 26, 961). The presence of 0.11% of cobalt had no effect. Tin affected the recovery profoundly, 0.25% moving the recovery range upward by more than

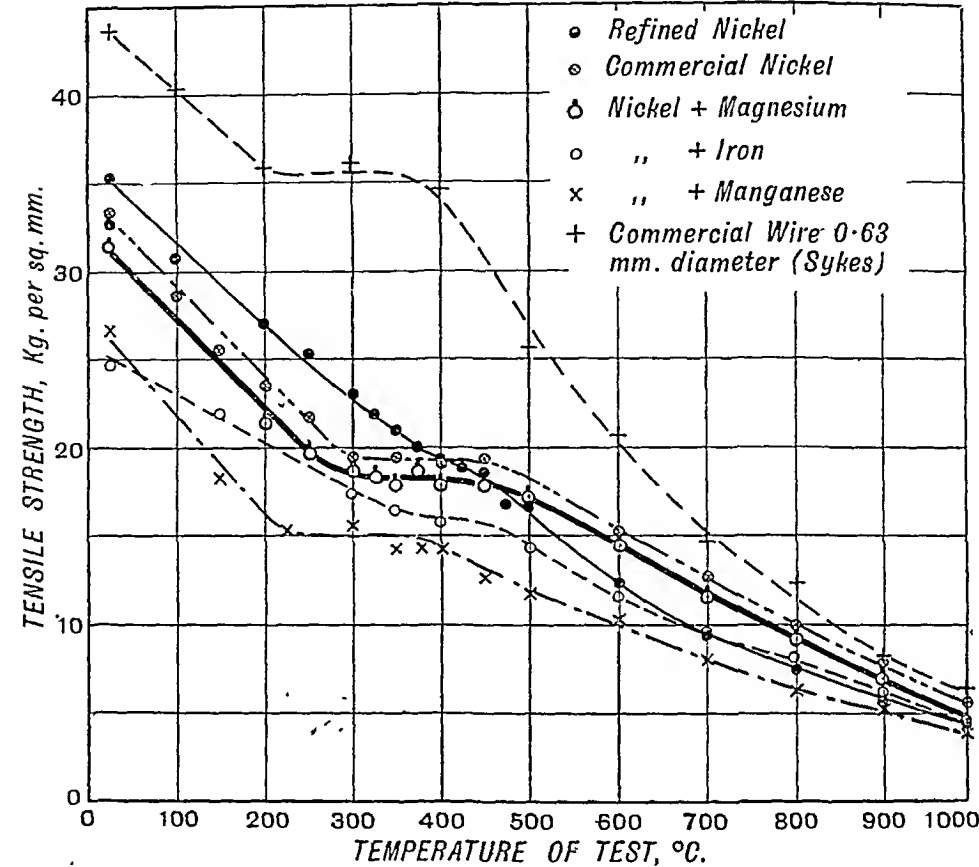


Fig. 7.

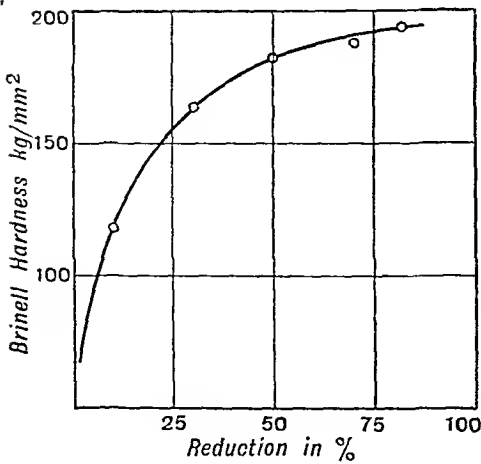


Fig. 8.

200°C. Additions of 0.25 and 0.75% of silicon raised the range 100° and 140°C. respectively. The action of copper was mild; the presence of 0.75% raised the softening temperature of

severely cold-worked carbonyl nickel by only 50°C.

TABLE VII.—COMPRESSIVE AND IMPACT PROPERTIES OF NICKEL.

Condition.	Compression.		Brinell hard- ness, 3,000 kg.	Izod, ft. lb.	Charpy, ft. lb.
	Yield strength, tons per sq. in.				
	0.1% perma- nent set.	0.2% perma- nent set.			
Hot rolled.	9.6	10.3	107	120	200
Cold drawn, 24% red- uction, stress re- lieved 3 hours at 300°o. .	24.6	26.0	177	120	204
Cold drawn, annealed 3 hours at 730°c. .	10.0	11.7	109	120	223

**Compressibility.**—Values for compression and impact properties of commercially pure nickel obtained by Catlin and Mudgo (Proc. Amer. Soc. Testing Materials, 1938, 38, 269) are given in Table VII.

**Modulus of Elasticity.**—The modulus of elasticity of nickel has been determined by several workers and varies between 21,000 and 23,000 kg. per sq. mm. (29,000,000–32,000,000 lb. per sq. in.).

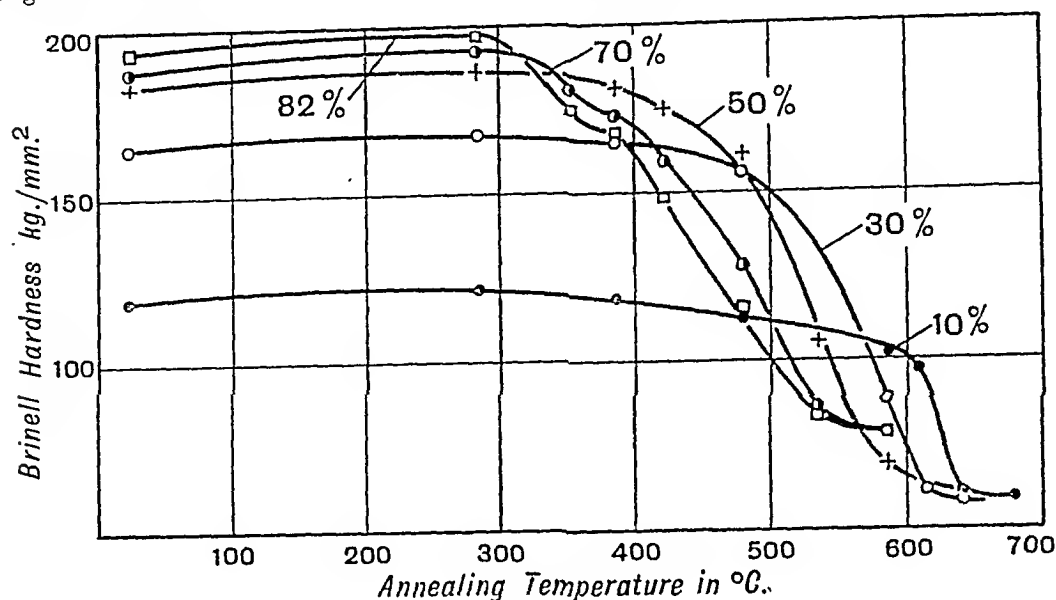


Fig. 9.

**Poisson's Ratio.**—Bonton (Physical Rev. 1900, [ii], 12, 36) gives Poisson's ratio for nickel as 0.33. Wise and Schaeffer (Met. and Alloys, 1942, 16, 424) give the figure 0.31, based on work by Vose.

#### CHEMICAL COMPOUNDS OF NICKEL.

**Nickel Oxides.**—The monoxide (NiO), found native as *bunsenite*, is the chief oxide of nickel. It may be prepared by calcining the carbonate, nitrate, hydroxide, chloride, bromide, iodate, or chlorate; or by heating nickel with a neutral solution of sodium sulphate at 200°C. It is also obtained by the electrolysis of a solution of a nickel salt and sodium acetate, the oxide forming at the anode.

Nickel oxide is a green crystalline powder, the shade varying with the method of preparation. When heated the oxide turns yellow. It is reduced by heating in hydrogen. The commoner salts are prepared from the monoxide. Commercial black oxide, prepared at a relatively low temperature, dissolves in acids much more quickly than oxides produced at higher temperatures.

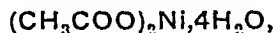
Several suboxides have been described by various investigators but their identity is doubtful. Nickelic oxide ( $\text{Ni}_2\text{O}_3$ ), obtained by gently heating the carbonate in air, is believed to be a combination in variable proportions of the monoxide and the peroxide,  $\text{NiO} \cdot \text{NiO}_2$ .

**Nickel dioxide or nickel peroxide ( $\text{NiO}_2$ )** may be obtained in the hydrated form by the action of hypochlorites on the monoxide in an alkaline solution. The dioxide dissolves in acids, forming nickelous salts. With sulphuric acid it forms nickelous sulphate; with hydrochloric acid it forms chlorine.

Salts of a hypothetical trioxide,  $\text{NiO}_3$ , have been reported. Hollard (Compt. rend. 1903, 136, 229) prepared a tetroxide ( $\text{NiO}_4$ ) by electrolysis. There is some doubt as to the existence of some of the higher oxides of nickel which have been reported; the monoxide and the dioxide are the only two oxides of importance.

Nickel oxide is used as a colour and ground coat constituent in pottery and vitreous enamelling and for the preparation of a catalyst in fat hardening. It is also used for the production of other nickel salts.

**Nickel Acetate.**—Nickel acetate,



is obtained by dissolving nickel or the oxide in acetic acid and evaporating. The acetate is precipitated as a green crystalline mass or powder. It is soluble in water but insoluble in alcohol.

This salt finds limited use in electroplating solutions, and as a mordant in printing cotton goods and dyeing.

**Nickel Bromide.**—Nickel bromide,  $\text{NiBr}_2$ , may be prepared by dissolving nickel hydroxide in hydrobromic acid, or by heating finely divided nickel in bromine vapour. The colour of this salt varies from a straw yellow to a dark brown. If heated, it turns a gold colour, and at higher temperatures sublimes in golden scales. This salt is very hygroscopic and forms a trihydrate  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ . Nickel bromide is soluble in hydrochloric acid and decomposes in nitric acid. It can be reduced by hydrogen, the reaction being reversible.

**Nickel Carbonate.**—Nickel carbonate,  $\text{NiCO}_3$ , is obtained by heating a solution of nickel chloride with calcium carbonate at 150°C.

The anhydrous carbonate forms pale green, transparent, microscopic rhombohedra.

The hexahydrate,  $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ , is obtained by mixing sodium or ammonium bicarbonate and a solution of nickel nitrate. The hexahydrate readily loses water. The pale green precipitates obtained by the addition of an alkali carbonate to a nickel salt are basic carbonates; the compositions vary according to the precipitant used and other factors.

Nickel carbonate is insoluble in water but is soluble in dilute mineral acids and in a solution of ammonium carbonate. Pale green insoluble flakes of ammonium nickel carbonate are precipitated from the latter on exposure to air.

The carbonate is used as a colour in ceramics and glazes, for the preparation of a catalyst in fat hardening, and in plating.

**Nickel Carbonyl.**—The production, properties, and uses of nickel carbonyl were described by R. L. Mond (J.S.C.I. 1930, 49, 271) and later by Trout (J. Chem. Educ. 1937, 453, 575). The compound at normal temperatures exists as a colourless liquid with a specific gravity of 1.38 and the rather high coefficient of expansion of 0.0018. The solid melts at  $-25^\circ\text{C}$ ., and the boiling-point of the liquid is  $44^\circ\text{C}$ . The vapour density was determined, by Victor Meyer's method, by L. Mond and his collaborators, who obtained a value of 86.7 at  $50^\circ\text{C}$ . Increased temperature makes the liquid unstable. Dewar and Jones (Proc. Roy. Soc. 1903, 71, 427) found that slight dissociation began at  $63^\circ\text{C}$ ., and it appeared to be almost complete at  $155^\circ\text{C}$ . at atmospheric pressure. They found increase of pressure decreased decomposition. Mittasch (Z. physikal. Chem. 1902, 40, 1), who obtained similar results, found traces of air to inhibit the reaction, the effect being counteracted by small amounts of hydrogen sulphide and accelerated by traces of mercury. He gave the heat of formation as 43.36 g.-cal. per g.

Nickel carbonyl is diamagnetic. Oxley (Proc. Camb. Phil. Soc. 1911, 16, i, 102) found the value for the magnetic susceptibility to be  $-4.81 \times 10^{-7}$ . Its refractive and dispersive powers are very high. Mond and Nasini (Z. physikal. Chem. 1891, 8, 154) gave the molecular refraction as 58.63 and the coefficient of dispersion as 1.1236.

The vibrational spectrum and the thermodynamic properties of nickel carbonyl were discussed by Crawford and Cross (J. Chem. Physics, 1938, 6, 525).

Oxidising agents such as nitric acid, chlorine, or bromine attack the carbonyl. Dewar and Jones (J.C.S. 1904, 19, 5) found that it was completely decomposed by solutions of the halogens and by those of the cyanogens and sulphur. The liquid may be distilled without decomposition. No compound of nickel carbonyl is known.

Apart from its use in nickel refining, the carbonyl has no important commercial use.

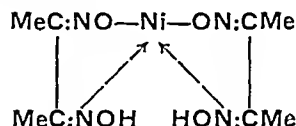
**Nickel Chloride.**—Nickel chloride,  $\text{NiCl}_2$ , is formed when finely divided nickel is heated in chlorine. It is also obtained by heating nickel sulphide with chlorine, when chlorides of nickel and sulphur are sublimed. The nickel chloride forms golden, crystalline scales. It dissolves in

water, with the evolution of heat, and a green hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) can be crystallised out from the solution. The anhydrous chloride absorbs ammonia, forming a near-white compound,  $\text{NiCl}_2 \cdot 6\text{NH}_3$ , which is soluble in water. Nickel chloride is reduced by heating in hydrogen. If heated in a current of air and hydrogen chloride, chlorine is evolved, so that this salt can replace the copper salt used in Deacon's process for chlorine.

Nickel chloride is employed as a colour for pottery, as a catalyst for the purification of coal gas, in electroplating solutions, and as an absorbent of ammonia in gas masks.

**Nickel Cyanide.**—Nickel cyanide,  $\text{Ni}(\text{CN})_2$ , is precipitated as apple-green plates or powder if potassium cyanide is added to a solution of nickel salt. It loses its water of crystallisation at  $200^\circ\text{C}$ . and decomposes on further heating. It is readily soluble in solutions of potassium cyanide and ammonium hydroxide. The double salt,  $\text{Ni}(\text{CN})_2 \cdot 2\text{KCN}$ , can be crystallised from a solution if potassium cyanide is added in excess. This salt is decomposed by dilute acids.

**Nickel Dimethylglyoxime.**—Nickel dimethylglyoxime,



is probably the commonest form in which nickel is precipitated and weighed in assaying. It is a scarlet powder and may be obtained by adding a solution of dimethylglyoxime in alcohol to an ammoniacal solution of a nickel salt. It is insoluble in water, acetic acid, and ammonia, but soluble in absolute alcohol.

**Nickel Fluoride.**—Nickel fluoride,  $\text{NiF}_2$ , is prepared by evaporating a solution of the carbonate in hydrofluoric acid. The fluoride crystallises in elongated, yellowish-green prisms. It is almost insoluble in water. By heating in hydrogen it is reduced to metal. If heated in air it is converted to oxide. Nickel fluoride is used to a limited extent in electroplating solutions.

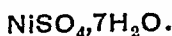
**Nickel Nitrate.**—Nickel nitrate,  $\text{Ni}(\text{NO}_3)_2$ , is produced by dissolving nickel, the oxide, or the carbonate, in nitric acid. On evaporation the hydrated salt is obtained in monoclinic crystals. This salt is soluble in both water and alcohol.

Anhydrous nickel nitrate is a greenish-yellow powder. The hexahydrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , forms in emerald-green plates. Several other hydrates exist.

The salt has a limited use for the preparation of a catalyst in fat hardening and as a colour in vitreous enamels.

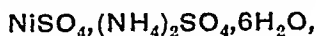
**Nickel Sulphate.**—Nickel sulphate,  $\text{NiSO}_4$ , occurs native as *morenosite*, identified by a deep-green efflorescence which Cronstedt observed on nickel-copper ores. It is also found in acicular crystals, thin prisms, and fibrous forms. The salt is formed by dissolving nickel, the hydroxide, or the carbonate, in dilute sulphuric acid, eva-

poration at normal temperatures giving emerald-green crystals of the heptahydrate,



Nickel sulphate is soluble in water. The percentage solubility, as given by Steele and Johnson (J.C.S. 1904, 85, 113) is 21.4, 30.2, 34.5, 43.3, and 46.5 at 0°, 31.5°, 53.3°, 99°, and 100°C., respectively. The solid phase changes at 31.5° from  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  to  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ . The monohydrate is insoluble in alcohol and ether, but the heptahydrate is soluble in alcohol. The chief use for the single salts is in electroplating; they are also used in the manufacture of paints, varnishes, ceramics, in the blackening of brass and zinc, and as a mordant in dyeing and printing textiles.

Nickel sulphate forms double sulphates with the sulphates of many other metals. Nickel ammonium sulphate,



which is used in electroplating, is the most important of the double sulphates. It is produced by dissolving the monoxide in sulphuric acid and adding ammonium sulphate to a concentrated solution. It is purified by recrystallisation, and forms bluish-green prisms.

## CORROSION RESISTANCE OF NICKEL.

Nickel occupies a position next to the brasses and bronzes in the electromotive series. It does not cause the emission of hydrogen from the commoner acids and the presence of some oxidising agent, such as dissolved air, is necessary for corrosion to proceed. As a rule, oxidising conditions accelerate the corrosion of nickel and reducing conditions retard it. Under some forms of attack nickel develops a corrosion-resisting or passive oxide film, so that corrosion is not always accelerated by oxidising conditions.

**Atmospheres.**—When used indoors nickel remains fairly free from tarnish, but when exposed outdoors it acquires a thin, adherent coating, usually a basic sulphate. In rural or marine atmospheres, attack is slow; in industrial districts the presence of sulphur has an accelerating effect.

**Waters.**—Both fresh water and sea water attack nickel very slowly. Stagnant exposure, where pockets of fluid occur, may cause pitting or localised corrosion.

**Salt Solutions.**—Neutral or alkaline salt solutions have only a slight effect on nickel, which is frequently used in contact with acetates, carbonates, chlorides, nitrates, and sulphates. Oxidising salt solutions, whether acid or alkaline, are corrosive, and even weak solutions of the chlorides of iron, mercury, and copper, in the presence of chromates, nitrates, and peroxides, cause serious corrosion.

**Acids.**—Nickel is often used in contact with sulphuric acid solutions, but it is attacked at all concentrations. Maximum attack occurs with 5% acid concentration, and decreases uniformly with increasing acid concentrations up to about 80% acid. Above this point corrosion rates are high. Both hydrochloric and phosphoric acids corrode nickel, the former rather rapidly under

most conditions. Oxidising compounds often present in commercial phosphoric acid, accelerate corrosion. Sulphurous acid solutions corrode nickel rapidly. Sulphur dioxide, often used in small percentages for the preservation of food products, produces a dark tarnish. The presence of hydrogen sulphide in solutions tends to increase corrosion; this is noted particularly in the case of brines.

Nitric, nitrous, and other oxidising acids corrode nickel rapidly. The presence of ferric and cupric salts, peroxides, and chromates also results in high corrosion rates.

Acetic, malic, tartaric, formic, and other organic acids at normal temperatures and in low concentrations do not corrode nickel unduly. High temperatures and aeration increase the rate of attack; hot solutions usually cause pitting. Stearic, oleic, and other fatty acids are moderately corrosive.

**Alkalis.**—Nickel is almost completely resistant to alkali attack. The rate at which nickel corrodes when in contact with highly concentrated sodium hydroxide solution depends on the early formation of a thin, dark, oxide film, which usually develops at temperatures above 300°C. Below 200°C. a green oxide film, with no protective properties, may be formed. With the dark film, corrosion rates are low. The presence of sulphur accelerates corrosion.

Anhydrous ammonia does not corrode nickel, but aqueous ammonia and ammonium hydroxide are very corrosive, except in concentrations under 1%.

**Gases.**—Nickel is resistant to attack by dry gases at normal temperatures, but if moisture is present sulphur dioxide, ammonia, nitrogen oxides, chlorine, and other halogens are corrosive. Sulphur gases attack nickel above about 350°C., especially in a reducing atmosphere. Sulphur dioxide is less corrosive to an alloy of nickel and 4% of manganese.

**Steam.**—Normally, steam does not corrode nickel below about 400°C., but at higher temperatures intercrystalline attack occurs. The carbon dioxide content of the steam is an important factor.

**Molten Metals.**—Nickel has no useful resistance to molten metals, but at temperatures under about 350°C. it may be used in contact with mercury. Cracking in locally stressed areas is likely unless the metal has been given a "stress-relief" anneal.

## NON-TOXICITY.

The physiological action of nickel has been studied by many workers from different viewpoints. Bertrand and Mokraguatz (Compt. rend. 1922, 175, 112, 458) examined twenty raw foodstuffs and found nickel to be present in all, the content ranging from 0.01 mg. per kg. in tomatoes to 2 mg. per kg. in peas. Nickel has also been found in various organisms, mosses, and plants. Lehmann (Arch. Hyg. Bakt. 1909, 73, 421) investigated the solubility of nickel and came to the conclusion that if all food were cooked in nickel the total quantity absorbed would be insignificant. Experiments with cats and dogs showed that no ill-effects

resulted when proportionately much larger quantities were absorbed. In a report to the Committee of the Royal Society on "Fats and Fatty Acids as Foods," Cushny stated, "Minute traces of nickel in hydrogenated fats are not injurious to health. Nickel is among the most harmless of metals." Pratt (*J. Nutrition*, 1930, 3, 141) investigated the action of nickel on vitamins and stated it had no destructive effect. He observed that nickel dissolved from nickel milk containers had no catalytic effect on the destruction of vitamins-A, -B, and -C. Nathan (*Zentr. Bakt.* 1904, 12, [ii], 93) stated that nickel had a slightly injurious action on fruit musts, but the polished metal had no injurious action on apples or beer wort, although the colour of the latter was changed. Various workers have observed that weak solutions of nickel chloride inhibit the growth of bacteria. Du Bois (*Schweiz. Med. Wochschr.* 1931, 21, 278) noted that nickel dermatitis caused by vapours from hot plating baths occurs with 95% of the workers employed. Attack is rare when cold solutions are used. Lanolin on the skin is a preventative.

### USES OF NICKEL.

**Malleable Nickel.**—Wrought nickel is chiefly employed for coinage, food, and chemical plant, and for anodes and cathodes in wireless receiving valves. Nickel is an excellent coinage metal. It is resistant to wear and corrosion and so tough that it cannot be counterfeited easily. Moreover, as it is magnetic, any counterfeit in a non-magnetic material could be readily detected.

**Electrodeposition.**—Electrodeposited nickel is one of the most widely used protective coatings on both ferrous and non-ferrous metals. Current practice is to use coatings of a thousandth (0.001) of an inch, usually flashed with chromium. The presence of a good underlay is essential for successful chromium plating, as too thin an underlay strips in the bath. The building up of worn parts by electrodeposition has been developed extensively. Coating by spraying is an alternative method of application. Automobile manufacturers are large users of plating anodes and have carried out, or inspired, many of the recent improvements in plating technique.

**Nickel Catalysts.**—Nickel, as a salt or in the form of metal turnings, is used to catalyse the hydrogenation of unsaturated organic compounds, notably for the production of solid edible fats from cotton-seed and peanut oils in the manufacture of margarine (*v.* Vol. VI, 177b). Other uses for nickel catalysts occur in oil refining, in the synthesis of ammonia and nitrates from nitrogen and its oxides, of alcohols from oxides of carbon, and of the higher hydrocarbons from acetylene. Two new processes for desulphurising coal gas are also based on the use of nickel catalysts (*v.* Vol. V, 466a).

**Nickel Steels.**—Wrought and cast alloy steels containing nickel are widely specified where the combination of high strength and toughness is needed. Used alone, or with one or more of the carbide-forming elements, such as

chromium and molybdenum, nickel permits the production of steels having a high strength to weight ratio, with good resistance to wear and fatigue. By suitable heat-treatment, tensile strengths exceeding 100 tons per sq. in. can be obtained in the more complex steels. With substantial alloy additions, excellent heat and corrosion-resisting properties are obtained.

Heat-treated nickel alloy steels are extensively used in the manufacture of automobile and aero engines, machine tools, and agricultural machinery, and in general engineering and ordnance. Steels in the normalised condition are employed in locomotive and bridge construction. The heat- and corrosion-resisting types have innumerable uses in many industries (*see also* Vol. VII, 48).

**Nickel Silvers.**—The alloys of nickel, zinc, and copper, usually known as nickel silvers, represent one of the oldest and most substantial uses for the metal. The white colour is obtained with 18–22% of nickel, but compositions containing down to 8% of nickel are often used for key metal and low-priced articles. Nickel silver is used as a base for silver-plated tableware and for plumbing and architectural metalwork.

**Nickel-Iron Alloys.**—Several special nickel-iron alloys have important, although limited, uses. Those containing 25–30% of nickel, cooled at normal rates, are non-magnetic and are used in the electrical industry. With a nickel content of about 36% a low coefficient of linear expansion is obtained; this type is used in horology. With about 40–50% of nickel, the coefficient of expansion is similar to that of glass, and the alloy is useful for lead-in wires for electric lamps. Alloys containing between 50 and 78.5% of nickel have high magnetic permeability at low field strengths and are used in radio, submarine-cable, and telephone communications.

**Nickel-Copper Alloys.**—Cupro-nickels containing about 20–30% of nickel have good ductility, toughness, and cold-working properties, and are resistant to corrosion. The 70/30 composition is used for condenser tubes. Alloys containing about 45% of nickel are employed for electrical resistances. The most important of these binary alloys is "*Monel*" (*v.* this Vol., p. 231a).

**Electrical Resistance Alloys.**—Nickel-chromium and nickel-chromium-iron alloys are almost universally employed for electrical resistance purposes in electric fires, furnaces, and domestic apparatus. The ternary alloy, employed in furnace construction, is now frequently used for chemical plant.

**Nickel Cast Iron.**—Small percentages of nickel improve the quality of grey iron in suitably adjusted compositions, producing a finer-grained structure with high strength and greater uniformity of properties. Increasing the nickel content improves wear and abrasion resistance, and used in conjunction with chromium, produces extremely hard martensitic irons suitable for rolls and crusher jaws. Austenitic cast irons for corrosion and heat-resisting purposes and heat-treatable types which can be hardened and tempered are now widely used in the automobile and metal working trades.

**Other Uses.**—There are numerous alloys which contain small percentages of nickel and are widely used. Many brasses, bronzes, and aluminium alloys come in this category. In other alloys, which have a limited use, the nickel addition may be substantial, as in nickel-iron-aluminium permanent magnet materials (v. *MAGNETIC ALLOYS*, Vol. VII, 456c), white gold, and die-casting alloys. There are about 1,000 nickel-containing trade-marked alloys on the market.

A. E. H.

**NICKEL MINERALS.** Nickel constitutes 0.016% of the first ton-mile depth of the earth's crust and occupies about 24th place in the frequency-sequence of elements. More than 85% of the nickel of commerce is obtained from ores containing nickel sulphides associated with iron and copper sulphides, the remainder coming largely from hydrous nickel silicate ores.

The principal ore mineral is *pentlandite*, a sulphide of iron and nickel,  $(\text{Fe}, \text{Ni})_9\text{S}_8$ , usually with Fe:Ni approximately 1:1, the nickel content averaging 34.5%. Small amounts of cobalt are usually present. According to the latest edition of Dana's "System of Mineralogy" (1944), the formula usually given for pentlandite,  $(\text{Fe}, \text{Ni})\text{S}$ , is erroneous. Among the silicate ores the chief mineral is the apple-green hydrous nickel magnesium silicate, *garnierite*, perhaps  $(\text{Ni}, \text{Mg})\text{SiO}_3 \cdot n\text{H}_2\text{O}$ , but very variable in composition, particularly as regards the nickel:magnesium ratio. It is seldom homogeneous, and may be accompanied by nickel-bearing nontronite and heidellite. Minor amounts of nickel are obtained from *niccolite*,  $\text{NiAs}$ , *millerite*,  $\text{NiS}$ , and from the light green bloom of secondary origin, *annabergite*,  $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ .

The great deposits of Sudbury, Ontario, dominate the world nickel production, having yielded about 85% of the entire global output during the past decade. In these deposits nickel is present almost wholly as pentlandite, in intimate association with pyrrhotite,  $\text{Fe}_{9}\text{S}_{11}$ , and chalcopyrite,  $\text{CuFeS}_2$ , the ores averaging about 1.5% nickel and 2% copper. The ore-bodies lie along or near the base of a thick sheet of norite, a basic igneous rock often referred to as the "nickel eruptive." Similar sulphide deposits occur near Petsamo in Finland, Norway, and the U.S.S.R. In New Caledonia, which ranks next to Sudbury in nickel production, there are shallow deposits containing garnierite in a weathered mantle of serpentinite derived by alteration of nickel-bearing peridotites, in which the nickel is originally present as a constituent of olivine. The average ore now smelted contains about 5% of nickel. Analogous silicate ores are also mined at Ufaloi and elsewhere in the Urals, and on the island of Celebes in the Netherlands East Indies.

During the past 25 years the world output of nickel has more than trebled, reaching about 125,000 tons in 1940, of which Ontario provided nearly 80%, New Caledonia 13%, and the Soviet Union about 3%. Nickel is essentially an alloy metal, mostly used in the manufacture of special steels, either alone or in addition to chromium, manganese, and other ferro-alloy metals. It

has been estimated that in 1939 the consumption of nickel was as follows: steels (including constructional, stainless, corrosion- and heat-resisting, and castings), 60%; nickel-copper and nickel silvers, 10%; "*Monel*," nickel-clad, "*Inconel*," etc., 10%; electrodeposition, 8%; nickel cast-iron, 3%; heat-resistant and electrical resistance alloys, 3%; nickel brass, bronze, and aluminium alloy castings, 2%; other uses, 4%. Since that date the proportion of nickel utilised in steel and foundry work has increased.

D. W.

**NICOTINAMIDE.** Pyridine-3-carboxyl-amido. Used for prophylaxis and treatment of pellagra, usually with other factors of the vitamin-B complex. B.P. Add. VI., B.P.C. (6th Supplement) (v. this Vol., p. 480a, and *SYNTHETIC DRUGS*).

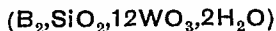
S. E.

**NICOTINE**,  $\text{C}_{10}\text{H}_{14}\text{N}_2$ , is a liquid, volatile alkaloid occurring in tobacco (*Nicotiana tabacum* Linn., and *N. rustica*) as citrate and malate, together with small amounts of *anabasine* (v. Vol. I, 365d) and 1-nornicotine,  $\text{C}_9\text{H}_{12}\text{N}_2$  (Ehrenstein, Arch. Pharm. 1931, 269, 627; Späth and Keszler, Ber. 1937, 70 [B], 704), *nicotyrine*,  $\text{C}_{10}\text{H}_{10}\text{N}_2$  (Wenusch, Biochem. Z. 1935, 275, 361; Späth and Keszler, Ber. 1937, 70 [B], 2450), and other alkaloids. Partially racemised d-nornicotine occurs in *Duboisia hopwoodii* F. Muell. (Späth, Hicks, and Zajic, *ibid.* 1935, 68 [B], 1388; 1936, 69 [B], 250). Tobacco contains, as a rule, from 1 to 8% of nicotine, but by far the greater proportion of commercial tobacco contains not more than 4% (v. *TOBACCO*).

**Preparation.**—Nicotine and tobacco extract are largely used as insecticides, and a considerable industry has been developed in the manufacture of these products from waste tobacco, and from the liquors obtained in the manufacture of chewing tobacco. Reid (Chem. and Ind. 1931, 50, 954) estimates the world production at 500 tons per annum. Extraction of the tobacco with water, usually in a continuous extraction apparatus, and concentration of the resulting liquor affords tobacco extract, and this is treated with lime or other alkali and steam-distilled. The crude nicotine is extracted from the distillate with ether or other organic solvent, or the distillate is neutralised with sulphuric acid and concentrated to yield commercial nicotine sulphate. R. Hofmann (Chem.-Ztg. 1934, 58, 700; G.P. 593259, Jan. 26th, 1933) recommends as an economical method adsorption of the nicotine from the vapours of the steam distillation by a suitable charcoal (made from tobacco waste), followed by elution with an organic solvent.

**Estimation.**—The majority of the methods employed involve a preliminary steam distillation of the nicotine from an extract containing a slight excess of alkali, this procedure serving to separate nicotine from most other alkaloids. The nicotine may be estimated in the distillate by direct titration with 0.1 N. sulphuric acid, using Methyl Red or iodoosin as indicator (Kissling, Z. anal. Chem. 1882, 21, 75; Schiok and Hatos, Z. Nahr. Genussm. 1914, 28, 269), but the silicotungstate method (Bertrand and Javillier, Bull. Soc. chim. 1909, [iv], 5, 241) is

usually preferred, since ammonia does not interfere. The distillate is made 0.5% in hydrochloric acid, and silicotungstic acid is added. The precipitate is collected after 24 hours, washed with cold 0.1% hydrochloric acid and ignited at ca. 800°. The weight of the residue ( $\text{SiO}_2 \cdot 12\text{WO}_3$ ), multiplied by 0.114, gives the weight of nicotine ("Official and Tentative Methods of Analysis of the Assoc. Off. Agric. Chem.," 4th ed. 1935, p. 60; Avens and Pearce, Ind. Eng. Chem. [Anal.], 1939, 11, 505). Alternatively, the silicotungstate

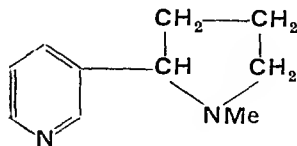


may be weighed after drying at 100° (Rapp, Woodmansee, and McHargue, J. Assoc. Off. Agric. Chem. 1942, 25, 760). Pfyl and Schmitt (Z. Unters. Lebensm. 1927, 54, 60) precipitate nicotine from the neutralised (Methyl Red) distillate as the dipicrate, which is collected and titrated with 0.1 N. sodium hydroxide in the presence of toluene and phenolphthalein. Polarimetric methods have been described by König (Chem.-Ztg. 1911, 35, 521), Tingle and Ferguson (Trans. Roy. Soc. Canada, 1916, [iii], 10, 27) and Tate and Warren (J.S.C.I. 1937, 56, 39T). Micro-determination can be effected by the silicotungstate method (Spies, Ind. Eng. Chem. [Anal.], 1937, 9, 46), colorimetrically (Sutherland, Daroga, and Pollard, J.S.C.I. 1939, 58, 284; Markwood, J. Assoc. Off. Agric. Chem. 1940, 23, 792) or turbidimetrically (*idem, ibid.*, p. 800). For estimation of nicotine in the presence of anabasine, see Shmuk and Borozdina (J. Appl. Chem. Russia, 1939, 12, 1585). Analytical methods have been reviewed by Tomkin ("Allen's Commercial Organic Analysis," 5th ed., 1929, Vol. VII, p. 625).

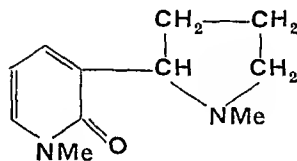
**Properties.**—Pungent, colourless, laevorotatory, hygroscopic liquid, b.p. 247°, which becomes brown in air owing to oxidation (*cf.* Ciamician and Silber, Ber. 1915, 48, 181). Distils unchanged in steam, in an atmosphere of hydrogen or nitrogen or *in vacuo*. For v.p. over the range 100–250°, see Gorbachev (J. Appl. Chem. Russia, 1934, 7, 388). Completely miscible with water below 60° and above 210°; between these temperatures miscibility is limited, the solubility curve having the form of a closed loop (Hudson, Z. physikal. Chem. 1904, 47, 113). Forms an azeotrope with water containing 2.5% nicotine, b.p. 99.988° (Smith, Ind. Eng. Chem. 1942, 34, 251). For partial v.ps. of nicotine and water over aqueous solutions at 25°, see Norton, Bigelow, and Vincent (J. Amer. Chem. Soc. 1940, 62, 261). Nicotine has  $\rho_4^{20} = 1.00925$  (Jephcott, J.C.S. 1919, 115, 104), increasing to 1.04 on addition of water up to 33% (Hudson, *l.c.*), and  $[\alpha]_D^{20} = -169.3^\circ$  (Lowry and Lloyd, *ibid.* 1929, 1771); its salts are dextrorotatory. Aqueous solutions are strongly alkaline; the salts crystallise with difficulty, but the dipicrate,  $\text{B}_2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , glancing yellow prisms, m.p. 224°, is characteristic. For microchemical identification, the formation of a crystalline precipitate with mercuric chloride, soluble in dilute acetic acid, is highly characteristic (Glycart, J. Assoc. Off. Agric. Chem. 1933, 16, 345; *cf.* Wenusch, Z. Unters. Lebensm.

1934, 67, 601). Nicotine and its salts are precipitated even in dilute solutions by the alkaloidal reagents.

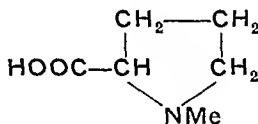
**Reactions and Constitution.**—Nicotine contains one N-methyl group, and reacts with methyl iodide as a tertiary base. On oxidation it yields nicotinic acid (this Vol., p. 479b), and hence contains a pyridine nucleus substituted at the  $\beta$ -position. Pinner (Ber. 1892, 25, 2807; 1893, 26, 292, 765) suggested the structure (I), and this has been proved correct by the oxidation of nicotine isomethiodide to N-methylnicotone (II) by means of potassium ferricyanide; chromic acid then yielded l-hygric acid (III) (Karrer and Widmer, Helv. Chim. Acta, 1925, 8, 364).



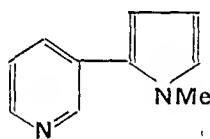
I.



II.

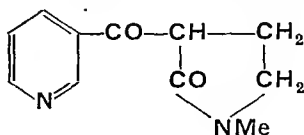


III.



IV.

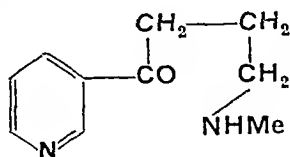
The structure (I) has been confirmed by synthesis. The original synthesis of nicotine by Pictet and collaborators (Ber. 1895, 28, 1911; 1898, 31, 2018; 1900, 33, 2355; 1904, 37, 1225), in which nicotyrine (IV) was an intermediate, involved the use of drastic conditions and hence did not afford a reliable proof of structure. Späth and Bretschneider (Ber. 1928, 61 [B], 327) condensed ethyl nicotinate with N-methylpyrrolidone to give a ketone (V), which on acid hydrolysis yielded the amino-ketone (VI). The latter was reduced to a secondary alcohol, which was converted to the corresponding iodo-compound; on standing in alkaline solution,



V.



this furnished *dl*-nicotine. A third synthesis has been described by Craig (J. Amer. Chem. Soc. 1933, 55, 2854), in which *nor*-nicotine is an intermediate.

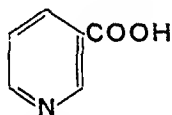


VI.

**Minor Alkaloids.**—The molecular structures of *nicotyrine* and *normicotine* follow from their relationship to nicotine, and from their syntheses. The former can be obtained from nicotine by the action of various mild oxidising agents, or by dehydrogenation over platinised asbestos at 320° (Wibaut and Overhoff, Rec. trav. chim. 1928, 47, 935). Its reduction to *dl*-nicotine, achieved with difficulty by Pictet (*l.c.*), has been effected more simply by controlled hydrogenation in presence of palladised charcoal (Späth and Kuffner, Ber. 1935, 68 [B], 494). *l*-*nor*-Nicotine has been obtained from nicotine by several demethylation processes (M. and M. Polonovski, Compt. rend. 1927, 184, 331, 1333; von Braun and Weissbach, Ber. 1930, 63 [B], 2018; Späth, Marion, and Zajic, *ibid.* 1936, 69 [B], 251); and is reconverted to nicotine on methylation (Späth and Zajic, *ibid.* 1935, 68 [B], 1667; Craig, *l.c.*).

H. T. O.

**NICOTINIC ACID**, "*Niacin*," pyridine-3-carboxylic acid,



was first obtained by Huber (Annalen, 1867, 141, 271) by oxidation of nicotine with chromic acid.

**Preparation.**—1. From nicotine by oxidation (Huber, *l.c.*; Laiblin, Annalen, 1879, 196, 135). A method suitable for the laboratory preparation, giving yields of 60% or better, uses concentrated nitric acid as the oxidising agent (McElvain, Organic Syntheses, Coll. Vol. I, 1932, p. 378).

2. By oxidation of  $\beta$ -picoline (Seyfferth, J. pr. Chem. 1886, [ii], 34, 258), 3-ethylpyridine (Ladenburg, 1896, 301, 152), 3-phenylpyridine (Skraup and Cobenzl, Monatsh. 1883, 4, 458) or 3:3'-dipyridyl (Skraup and Vortmann, *ibid.*, p. 594). For the technical preparation of nicotinic acid by this method, suitable starting materials are the base fractions b.p. 135–142° from coal-tar, petroleum, or bone-oil (Pinner, Ber. 1900, 33, 1227; Weidel, *ibid.* 1879, 12, 1992).

3. By decarboxylation of pyridine-polycarboxylic acids, notably quinolinic and isoquinolinic acids; this may be effected thermally (Hoogewerff and Van Dorp, Annalen, 1880, 204, 117) or by means of acids (Weidel and Herzog, Monatsh. 1885, 6, 982).

4. By synthesis from pyridine. Pyridine- $\beta$ -sulphonic acid, obtained by sulphonation of

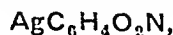
pyridine, is converted to nicotino-nitrile by standard methods and thence by saponification to the acid (Fischer, Ber. 1882, 15, 63). A 70% yield of nicotinic acid is obtained by carbonation of the product of reaction of butyl-lithium and 3-bromopyridine (Gilman and Spatz, J. Amer. Chem. Soc. 1940, 62, 446). For preparation of nicotinic acid in the laboratory, pyridine is brominated to 3-bromopyridine; this is then converted by distillation with cuprous cyanide to the nitrile, and the latter hydrolysed to nicotinic acid (McElvain and Goese, *ibid.* 1911, 63, 2283).

**Physical Properties.**—Nicotinic acid forms colourless needles from water or alcohol, m.p. 235.5–236.5° (Gordin and Flexser, J. Amer. Pharm. Assoc. 1940, 29, 230), readily soluble in hot water or hot alcohol, only very slightly so in ether. It sublimes undecomposed above 150°. Electrolytic dissociation constant  $1.58 \times 10^{-5}$  (Erlenmeyer, Epprecht, and Meyenburg, Helv. Chim. Acta, 1937, 20, 310); for the dielectric coefficient, see Devoto and Ardissoni (Gazzetta, 1935, 65, 1235); for the heat of neutralisation, see Devoto (Atti. R. Accad. Lincei, 1934, 19, 50). The absorption spectrum shows a maximum at 385 m $\mu$ . ( $\epsilon=3,800$ ) (Hünecke, Ber. 1927, 60 [B], 1451).

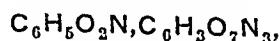
#### CHEMICAL PROPERTIES.

Nicotinic acid yields pyridine when the calcium salt is distilled with soda-lime (Weidel, Annalen, 1873, 165, 343). The location of the carboxyl group follows from the production of the acid by decarboxylation of both quinolinic and isoquinolinic acids; the structures of the latter are known from their formation from synthetic quinoline and isoquinoline respectively. In aqueous solutions of nicotinic acid, equilibrium exists between the true acidic form and the zwitterion, the former predominating (Devoto, Z. Elektrochem. 1934, 40, 490; Hünecke, *l.c.*; Kuhn and Brydówna, Ber. 1937, 70 [B], 1333). Reduction of nicotinic acid in alcoholic solution with sodium gives piperidine- $\beta$ -carboxylic acid (*nicotinic acid*); reduction in aqueous solution with sodium amalgam gives  $\alpha$ -hydroxynicotinic acid (Ladenburg, *ibid.* 1892, 25, 2768).

Nicotinic acid is amphoteric and forms salts with both acids and bases. The *basic copper salt*,  $\text{Cu}(\text{OH})\text{C}_6\text{H}_4\text{O}_2\text{N}$ , forms a bright blue insoluble precipitate; the *silver salt*,



needles from water (Laiblin, *l.c.*); the *calcium salt*,  $\text{Ca}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2 \cdot 5\text{H}_2\text{O}$ , is very insoluble in water. Nicotinic acid gives no precipitate with lead acetate. The *hydrochloride*,  $\text{C}_6\text{H}_5\text{O}_2\text{N} \cdot \text{HCl}$ , m.p. 273–274° (McElvain, *l.c.*) is soluble in alcohol; the *hydrobromide*,  $\text{C}_6\text{H}_5\text{O}_2\text{N} \cdot \text{HBr}$ , plates from water or alcohol, m.p. 275°, may be sublimed (Claus and Pylehau, J. pr. Chem. 1893, [ii], 47, 416); the *platinichloride*,  $2\text{C}_6\text{H}_5\text{O}_2\text{N} \cdot \text{PtCl}_4 \cdot 2\text{HCl} \cdot 2\text{H}_2\text{O}$ , has m.p. 253° (Drummond and Funk, Biochem. J. 1914, 8, 604); the *picrate*,



yellow rods from water, has m.p. 214° (decomp.) (Swzuki, Shemimura, and Otake, *Biochem. Z.* 1912, 43, 89).

Methyl Nicotinate prepared by the Fischer-Speier technique (Engler, *Ber.* 1894, 27, 1787), by the action of diazomethane on aqueous nicotinic acid, or by heating tetramethylammonium nicotinate (Prelog and Picentanida, *Z. physiol. Chem.* 1936, 244, 56) has m.p. 39°, b.p. 204°, and is soluble in water, alcohol, and benzene.

Ethyl Nicotinate has b.p. 223–224° (Camps, *Arch. Pharm.* 1902, 240, 353).

Nicotinyl Chloride, obtained by not too protracted boiling of the acid with thionyl chloride, has m.p. 15–16°, b.p. 85°/12 mm. (Méyer and Graf, *Ber.* 1928, 61 [B], 2205); the hydrochloride, m.p. 155.5–156.5°, sublimes in needles (Späth and Spitzer, *ibid.* 1926, 59 [B], 1479).

Nicotinic Anhydride, m.p. 122–124° (Graf, *Biochem. Z.* 1930, 229, 164), is only slowly hydrolysed by water.

### Nicotinamide.

Nicotinamide, or "*Niacinamide*," first obtained by Engler (*l.c.*) from methyl nicotinate and methyl alcoholic ammonia, can also be prepared by treating the ethyl ester with aqueous ammonia (LaForge, *J. Amer. Chem. Soc.* 1928, 50, 2477) or by treatment of the acid with ammonia gas at 230° (Keimatsu, Yokota, and Satoda, *J. Pharm. Soc. Japan*, 1933, 53, 994). It forms needles from benzene or chloroform, m.p. 129° (Kuhn and Vetter, *Ber.* 1935, 68 [B], 2374), is soluble in water, alcohol, and ether, and distills at 150–160°/5 × 10<sup>-4</sup> mm. The absorption spectrum shows two bands with maxima at 215 mμ. (ε=7,100) and 260 mμ. (ε=2,700) (Kuhn and Vetter, *l.c.*). Aqueous solutions of nicotinamide (and nicotinic acid) show yellow fluorescence in ultra-violet light (Hirt and Wimmer, *Klin. Woch.* 1939, 18, 765).

Heating with thionyl chloride or phosphorus pentoxide converts nicotinamide to *nicotinonitrile*, needles from ether-light petroleum, m.p. 50°, b.p. 240–250°, readily soluble in water, alcohol, or ether (Meyer, *Monatsh.* 1902, 23, 901; LaForge, *l.c.*). The action of bromine and potassium hydroxide on nicotinamide is complex, giving *inter al.*, 3-aminopyridine (Camps, *l.c.*).

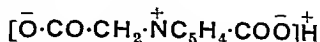
*Nicotinamide methiodide*, formed by boiling nicotinamide and methyl iodide has m.p. 204° (Karrer, Schwarzenbach, Benz, and Solmssen, *Helv. Chim. Acta*, 1936, 19, 811).

Numerous N-substituted nicotinamides are known: *nicotinmethylanilide*, needles from benzene, m.p. 104–105° (Pictet and Süssdorf, *Chem. Centr.* 1898, 1, 677); *nicotinanolide*, needles from benzene-ligroin, m.p. 132° (*idem*, *ibid.*). NN-Disubstituted nicotinamides, formed by action of phosphorus pentoxide on nicotinic acid and a secondary amine in a solvent (B.P. 450051), according to U.S.P. 1617332, have therapeutic activity; the most important is nicotindithethylamide ("*Coramine*," "*Nikethamide*").

Nicotinuric Acid, 3-pyridoylamino-acetic acid, obtained by treatment of the chloride or

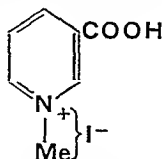
azide of nicotinic acid with glycine (Fox and Field, *J. Biol. Chem.* 1943, 147, 651), has m.p. 214–244°.

### Nicotinic Acid Betaine,

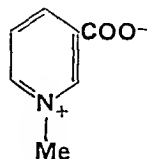


is obtained by boiling nicotinic acid with chloroacetic acid in dilute sodium hydroxide solution (Kirpal, *Monatsh.* 1910, 31, 972).

Nicotinic Acid Methiodide, obtained by action of methyl iodide on nicotinic acid and excess sodium hydroxide, forms crystals from alcohol-ether which blacken at 180°, m.p. ca. 220°, and is converted by treatment with silver oxide into trigonelline.



Nicotinic acid methiodide.



Trigonelline.

### NICOTINIC ACID (AMIDE) AS THE PELLAGRA-PREVENTATIVE VITAMIN.

Nicotinic acid is probably present (mostly in the combined state) in all living cells. It was isolated from rice-polishings in 1911 (Funk, *J. Physiol.* 1911, 43, 395; Suzuki, Shemimura, and Otake, *l.c.*) and from yeast by Vickery in 1926 (*J. Biol. Chem.* 1926, 68, 585); the amide was isolated from heart muscle in 1935 by Kuhn and Vetter (*l.c.*). In the same year, attention was drawn to the biological importance of nicotinamide by the discovery that it is an integral part of the molecules of cozymase (codehydrogenase I, disphosphopyridine nucleotide) and of codehydrogenase II (triphosphopyridine nucleotide) (Euler, Albers, and Schlenk, *Z. physiol. Chem.* 1935, 237, 1; Warburg and Christian, *Biochem. Z.* 1935, 275, 464).

In 1937 the essential nature of nicotinamide (or nicotinic acid) for micro-organisms, dogs, and humans was established. Supply of the acid or amide was found necessary for the growth of *Staphylococcus aureus* (Knight, *Biochem. J.* 1937, 31, 731) and the diphtheria bacillus (Mueller, *J. Biol. Chem.* 1937, 120, 219); the dietary factor curative of canine black-tongue, isolated from liver by Elvehjem, Madden, Strong, and Woolley (*J. Amer. Chem. Soc.* 1937, 59, 1767; *Dann, Science*, 1937, 86, 616) was shown to be identical with nicotinamide. The efficacy of the acid in the treatment of the analogous deficiency condition in humans (pellagra) was reported by Fouts, Helmer, Lepkovsky, and Jukes (*Proc. Soc. Exp. Biol. Med.* 1937, 37, 547; *cf.* Spies, Cooper, and Blankenhorn, *J. Amer. Med. Assoc.* 1938, 110, 622; Elvehjem, *Physiol. Rev.* 1940, 20, 249). The acid (or amide) therefore became identified with the pellagra-preventative (P-P) factor of the vitamin-B<sub>2</sub> complex. It may be remarked that pellagra is seldom due to dietary deficiency in nicotinic acid alone, and the importance of treatment by supplementary administration of other members of the vitamin-B<sub>2</sub> complex has

been emphasised (Vilter, Vilter, and Spies, J. Amer. Med. Assoc. 1939, 112, 420; Josephson and Klewan, Nature, 1939, 143, 725).

Other species for which nicotinic acid is a dietary essential are the pig (Chick, Macrae, Martin, and Martin, Biochem. J. 1938, 32, 10), the monkey (Harris, *ibid.*, p. 1479) and the chick (Koehn and Elvehjem, J. Biol. Chem. 1937, 118, 693). Rats can apparently synthesise nicotinic acid in their tissues (*see* Huff, Perlzweig, and Spilman, *ibid.* 1942, 142, 401).

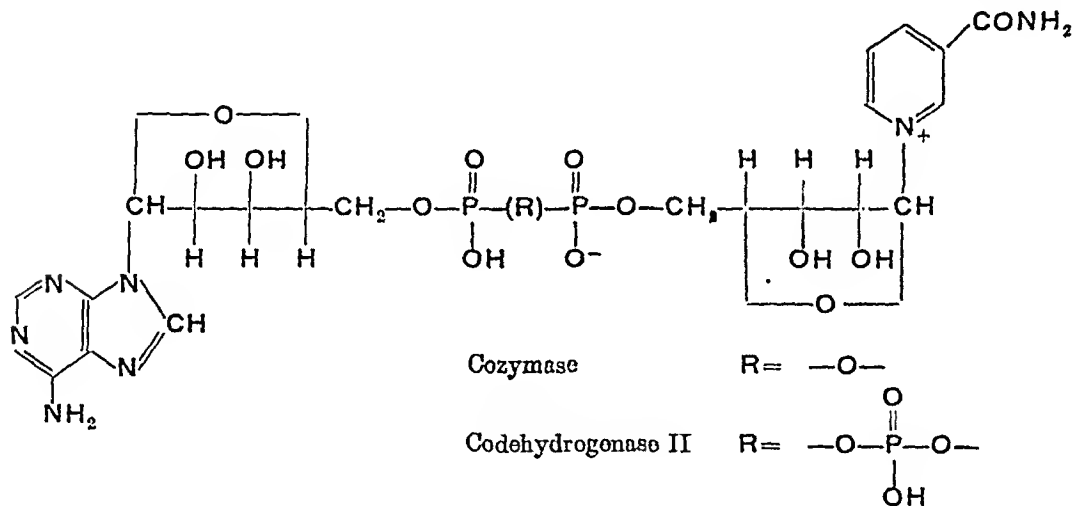
Nicotinic acid is needed by plants (Bonner, Plant Physiol. 1938, 13, 865) and by micro-organisms. Some of the latter (*e.g.*, *Chilomonas paramecium*) can synthesise their nicotinic acid requirements (Hutchings, Jandorf, and Hastings, *ibid.* 1941, 138, 321); M. Guggenheim ("Die biogenen Amine," New York, 1940), has suggested that biosynthesis of nicotinic acid takes place from ornithine or proline via  $\delta$ -aminovaleric acid and guvacin. Micro-organisms dependent on an external supply vary in their response to nicotinic acid derivatives. For the diphtheria bacillus, response is greater to the acid than to the amide; organisms of the *Pasteurella* group respond only to the amide; *Hæmophilus influenzae* and *H. parainfluenzae* require the whole codehydro-

genase (Factor V) molecule (Koser, Berkman, and Dorfman, Proc. Soc. Exp. Biol. Med. 1941, 47, 504; Schlenk and Gingrich, J. Biol. Chem. 1942, 143, 295). Nicotinic acid also stimulates growth of *H. pertussis* (Hornibrook, Proc. Soc. Exp. Biol. Med. 1940, 45, 598) and is required by organisms of the *Proteus* group (Pelczar and Porter, *ibid.* 1940, 43, 151; Morel, Ann. Inst. Pasteur, 1941, 67, 285).

**Specificity.**—Compounds exhibiting antipellagra activity are nicotinic acid and amide, methyl nicotinate, "coramine," and nicotinuric acid (Woolley, Strong, Madden, and Elvehjem, J. Biol. Chem. 1938, 124, 715), quinolinic acid, pyrazine carboxylic acid, and pyrazine-2:3-dicarboxylic acid (Vilter and Spies, Lancet, 1939, 2, 423). The three last mentioned are ineffective in treatment of canine blacktongue. Quinolinic acid and thiazole-5-carboxylic acid can replace nicotinic acid as growth factor for the dysentery bacillus.

#### Mechanism of Vitamin Action.

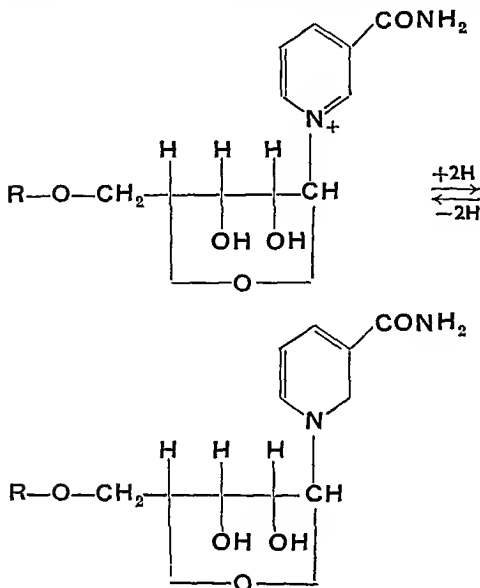
The vitamin activity of nicotinic acid and the amide is usually ascribed to the part they play in the cellular synthesis of cozymase and codehydrogenase II. These coenzymes are present in all living cells; in combination with



the appropriate specific protein (apoenzyme), they constitute the effective agents of hydrogen transport in many of the dehydrogenation reactions by means of which the *in vivo* oxidation of carbohydrate is accomplished (for details, *see* reviews by Baumann and Stare, Physiol. Rev. 1939, 19, 353; Barron, *ibid.* 1940, 20, 184). Elucidation of the function of the nicotinamide residue in the coenzyme molecule was aided by the discovery of the reversible oxidation-reduction behaviour of nicotinamide methiodide (Karrer, Schwarzenbach, Benz, and Solmsen, *l.c.*); the nicotinamide residue in the coenzyme molecule is endowed with the ability to take up from the substrate two atoms of hydrogen with formation of the dihydro-coenzyme; the latter then gives up the hydrogen atoms to a suitable acceptor with regeneration of the coenzyme molecule (Warburg, Christian, and Griese, Biochem. J., 1935, 282, 157). The wide

range of organisms requiring nicotinic acid indicates its function in some fundamental biochemical process, and analogous coenzyme function has been established for other B-vitamins (anurine and riboflavin). Supporting the view that nicotinic acid functions biologically as the pyridine nucleotides are (i) the requirement of the less synthetically versatile micro-organisms for the whole cozymase molecule, (ii) the observed synthesis from nicotinic acid of the pyridine nucleotides by micro-organisms and erythrocytes (Axelrod, Spies, and Elvehjem, J. Biol. Chem. 1931, 138, 667) and, (iii) the decrease from normal of the pyridine nucleotide content of striated muscle during pellagra in humans, and in liver and muscle in canine blacktongue. Part of the therapeutic activity of nicotinamide may be due to the specific inhibitory effect it exercises against breakdown of cozymase by cellular nucleotidases (Mann and

Quastel, *Biochem. J.* 1941, 35, 502). It is, however, improbable that death in blacktongue is caused by direct failure of tissue respiration due to decrease in coenzyme content. In this connection the dehydration and electrolyte imbalance in nicotinic acid deficiency in dogs are significant, pointing to dysfunction of the supra-



renal cortex as the immediate cause of death (Handler and Dann, *J. Biol. Chem.* 1942, 145, 145). This may, of course, be due to coenzyme deficiency, although intravenous administration to dogs with blacktongue of amounts of coenzyme which, on the basis of nicotinic acid content, would be expected to be beneficial, failed to effect a cure (Martin, Thompson, and Carvajal-Forero, *Amer. J. digest. Dis.* 1941, 8, 290). Since growth and respiration of dysentery bacilli are more favourably affected by the acid or amide than by intact coenzyme, Saunders, Dorfman, and Koser (*J. Biol. Chem.* 1941, 138, 69) conclude that nicotinamide is concerned in cellular oxidations in some way other than as di- and triphosphopyridine nucleotides.

### Physiology.

Nicotinic acid, the sodium salt, and the amide are used in treatment and prophylaxis of pellagra and have also been used successfully in treatment of many related clinical conditions. The daily requirement of humans is uncertain; 50–500 mg. daily, given orally, is the usual therapeutic dose; dogs require 200–365  $\mu\text{g}$ . daily for each kg. of body weight (Schaeffer, McKibbin, and Elvehjem, *ibid.* 1942, 144, 679). Nicotinic acid is of low toxicity, although in human subjects it may produce a transient vasodilation with sensations of flushing, burning, and itching; nicotinamide does not produce these effects. Large doses may be toxic; dogs receiving 2 g. per day died within 20 days. Nicotinic acid is excreted in the urine, partly as the free acid, but in man and dogs trigonelline, and to a lesser extent, nicotinuric acid, are the principal metabolic end-products (see Sarett

and Stenhouse, *J. Nutrition*, 1942, 23, 35). Methods suggested for assessment of status of nicotinic acid nutrition include assay of urinary excretion of trigonelline (Field, Melnick, Robinson, and Wilkinson, *J. clin. Invest.* 1941, 20, 379), and nicotinic acid excretion during 12–14 hours after administration of a 500 mg. dose (Perlzweig, Sarett, and Margolis, *J. Amer. Med. Assoc.* 1942, 118, 28).

### Determination of Nicotinic Acid Derivatives.

Methods have been developed for the assay of nicotinic acid in animal tissues, blood, urine, plant products, and foodstuffs. The methods employed can be considered under two principal headings.

(a) *Microbiological Methods.*—In these, the nicotinic acid present in an extract is estimated by the growth-response induced in a micro-organism cultured in a nicotinic acid-deficient basal medium. In the method using *Shigella paradysenteriae* as test-organism, growth stimulation is estimated turbidimetrically (Isbell, Wooley, Butler, and Sebrell, *J. Biol. Chem.* 1941, 139, 499); that using *Lactobacillus arabinosus* uses titration of lactic acid produced by the micro-organism as the measure of growth stimulation. The latter method has the advantage that removal of turbidity or coloured contaminants from extracts is unnecessary; the method estimates accurately as little as 1  $\mu\text{g}$ ., and has been applied to the assay of a wide variety of materials (Tepley, Strong, and Elvehjem, *J. Nutrition*, 1942, 23, 417). The method is not specific for nicotinic acid, equivalent growth-responses being given by nicotinamide, nicotinuric acid, and the pyridine nucleotides.

(b) *Chemical Methods.*—Of these, the most satisfactory are modifications of the König method (*J. pr. Chem.* 1904, [ii], 70, 109); an aqueous solution of the acid is treated with cyanogen bromide, when the pyridine ring is split to give a substance which on addition of an aromatic amine produces a coloured compound. The colour intensity, estimated conveniently by photoelectric colorimetry, is a measure of the nicotinic acid content of the solution. The reaction is not specific for nicotinic acid, colour being given by pyridine derivatives with unsubstituted  $\alpha$ -positions. A variety of aromatic amines have been used for the colour development (see Waisman and Elvehjem, *Ind. Eng. Chem. [Anal.]*, 1941, 13, 221). Difficulties encountered in the application of the chemical methods include: Need for a satisfactory extraction of the assay material; need for conversion of nicotinic acid derivatives to the free acid; need for removal from extracts of coloured and other contaminants which interfere with the assay; the instability of the colour, and interference with its development by salts; need for blank tests with reagents, etc. The various procedures are designed to take care of these factors.

For assay in tissues, the method of Dann and Handler (*J. Biol. Chem.* 1941, 140, 201) is convenient. The fresh tissue is ground with sand and water, extracted with hot hydrochloric acid, purified by adsorption on and elution from

Lloyd's reagent, impurities precipitated with lead hydroxide, and the nicotinic acid in the filtrate estimated by the cyanogen bromide method, using Metol for colour development. Nicotinic acid in plant tissues may be determined by the cyanogen bromide method provided that the aqueous tissue extract is hydrolysed with acid prior to treatment with the reagent (Hale, Davis, and Baldwin, *ibid.* 1942, 146, 553). For the determination in blood, see Klein, Perlzweig, and Handler, *ibid.* 1942, 145, 27; Allinson, *ibid.* 1943, 147, 785, in urine: see Melnick, Robinson, and Field, *ibid.* 1940, 136, 131, 145; Perlzweig, Levy, and Sarett, *ibid.*, p. 729; the methods described permit the separate determination of nicotinic acid (nicotinamide), nicotinuric acid, and trigonelline. For separate determination of "bound" nicotinic acid (*i.e.*, that present as the pyridine nucleotides), and "free" nicotinic acid in tissues, see Handler and Dann (*l.c.*); Axelrod, Spies, and Elvehjem (*l.c.*).

#### Nicotinic Acid Content of Foodstuffs.

Reference may be made to the following papers: Bacharach, *Nutr. Abs.* 1941, 10, 495; Tepley, Strong, and Elvehjem, *l.c.*; Snell and Wright, *Univ. of Texas Publication*, 1941, 4137, 22; Cheldelin and Williams, *ibid.* 1942, 4237, 97; Dann and Handler, *l.c.*; *idem*, *J. Nutrition*, 1942, 24, 153; McVicar and Berryman, *ibid.*, p. 235; McIntire, Waisman, Henderson, and Elvehjem, *ibid.* 1941, 22, 535; Hale, Davis, and Baldwin, *l.c.*

In the following table, various foodstuffs are classified in approximate order of their values as dietary sources of nicotinic acid.

Nicotinic acid content, mg. per 100 c.c.	Foodstuff.
55-30	Brewer's yeast; wheat bran.
30-15	Beef and hog liver; chicken breast muscle.
10-5	Salmon muscle; smoked ham; chicken leg muscle; beef and hog muscle; wheat; barley.
5-1	Molasses; soya beans; cod muscle; dried skim milk; spinach; oats; polished rice; dried peas; potatoes.
1-0.1	Cabbage; carrots.

Milk is a relatively poor source of nicotinic acid, containing *ca.* 80  $\mu\text{g.}/100$  c.c. Nicotinic acid content of meats is not appreciably decreased by cooking or commercial processing.

B. L.

#### "NICROSILAL" (*v.* Vol. VII, 37d).

**NIGELLA OIL**, Small Fennel or Black Cumin oil, is a reddish semi-drying oil of bitter taste and aromatic odour occurring to the extent of 35% in the seeds of *Nigella sativa* L. (Fam. Ranunculaceae). The following characteristics have been recorded:  $\rho_{15}^4$  0.925, saponification value 196.4-202, iodine number 107.4-116.2; Reichert-Meißl No. 3.4-5.4; solidifying point of fatty acids  $-16^{\circ}$  to  $-19^{\circ}$  (Crossley and Le Sueur, *J.S.C.I.* 1898, 17, 992; Bureš and Mladkova, *Casopis Českoslov. Lék.* 1928, 8, 186; 1930, 10, 317).

The seeds also yield 1% of a yellow essential oil of unpleasant odour, which gives no fluorescence, in contrast to that obtained from *Nigella damascena* which gives a blue fluorescence.

M. L. M.

**NIGER SEED OIL**. A drying oil obtained from the achenes of *Guizotia abyssinica* (Linn.) Cass (*Guizotia oleifera* DC.), a plant cultivated in East Africa, India, and the East and West Indies. Attempts have also been made to grow it in Germany. The achenes, which contain 40-45% of oil, are either cold or hot pressed to give an oil of  $\rho$  0.925-0.948, refractive index 1.472-1.477, iodine number 126.6-133.8, saponification value 189-192, free fatty acids, as oleic 2.5-6%.

The component fatty acids (wts.%) of Indian and African oil have been found to be, respectively, myristic 1.7, 1.1, palmitic 5.0, 7.2, stearic 2, 3.2, traces of higher saturated acids, oleic 38.9, 17, linoleic 51.6, 71.1 (N. L. Vidyarthi and M. V. Mallya, *J. Indian Chem. Soc.* 1940, 27, 87; T. P. Hilditch and I. C. Sime, *J.S.C.I.* 1944, 63, 112). The refined oil is used for edible purposes, cruder oil for soap making and as a substitute for linseed oil in paints.

M. L. M.

**NIGHT BLUE** is the triphenylmethane dye-stuff prepared from tetraethyldiaminobenzophenone and *p*-tolyl- $\alpha$ -naphthylamine. It forms insoluble compounds with Naphthol Yellow S and Pierie Acid, which may be used for the estimation of these substances.

G. W. K.

#### NIGROSINE (*v.* Vol. VI, 467d).

**NIIN**, a yellowish-brown fatty mass obtained by boiling hemipterous insects which feed on plants of the genus *Spondias* (Fam. Anacardiaceae) in Yucatan and Veraeruz. Schott (Chem. News, 1870, 22, 110; Report of the Commissioner of Agriculture, Washington, U.S.A. 1868, 268) records the following properties: m.p. about  $49^{\circ}$ ,  $\rho^{15}$  about 0.92, soluble in ether. A film of the fat when heated above  $120^{\circ}$  becomes tough and insoluble. A solution of the fat in oil of turpentine is a waterproofing medium and if exposed to air in thin layers for a few days it acquires the properties of a hard drying varnish.

J. N. G.

**NIKETHAMIDE**. Pyridine-3-carboxyldiethylamide. "*Coramine*." Circulatory and respiratory stimulant. B.P. Add. III., B.P.C. (*v.* SYNTHETIC DRUGS).

S. E.

#### NINHYDRIN (*v.* Vol. I, 324b; VI, 307d).

#### NIOBIUM (*v.* Vol. III, 309d).

#### "NIPAGIN" (*v.* Vol. VI, 346b).

#### "NIRESIST" (*v.* Vol. VII, 37d).

#### NISINIC ACID (*v.* Vol. III, 247b).

#### NITRALLOY (*v.* Vol. VII, 47d, 50a).

**NITRATINE**, Soda-nitric, or Chile saltpetre. Sodium nitrate,  $\text{NaNO}_3$ , is the most abundant and commercially important of the natural mineral nitrates, with potassium nitrate a very poor second. Nitratine crystallises in the rhombohedral system and is homeomorphous with calcite. Natural crystals are rare, the mineral being generally found as crystalline aggregates or grains, and as encrustations or widespread

deposits. Small rhombohedrons of nitratine can readily be grown artificially in a crystallising solution of sodium nitrate. They possess perfect rhombohedral cleavage and a double refraction even stronger than that of calcite. The natural mineral is colourless or white, also grey, yellow, and reddish-brown, and has a vitreous lustre. It varies from transparent to nearly opaque, has a cooling and saline taste, and is strongly deliquescent, besides being easily and completely soluble in water. It colours the flame intensely yellow, and when heated in a closed tube with potassium bisulphate it emits red vapours of nitrogen oxides. Hardness 1-2;  $\rho$  2.29.

Owing to its ready solubility nitratine is confined to arid and desert regions, the only large-scale commercial deposits occurring in the Atacama, Tarapacá, and Antofagasta regions of northern Chile. Here the "caliche" or nitrate bed occurs as a superficial deposit from a few inches to 14 feet thick, overlain by a shallow covering of sand, gravel, and gypsum. It contains about 25% of sodium nitrate, together with 2-3% of potassium nitrate, 8-50% of sodium chloride, and numerous sulphates, borates, bromides, and iodates. Of the several theories advanced to explain the origin of these puzzling deposits the most acceptable seems to be that which attributes the source of the nitrate to the leaching of nearby volcanic rocks under unusually arid conditions. The sodium nitrate is extracted from the caliche in the Shanks process by leaching at boiling temperatures, and in the Guggenheim process by filtering and leaching at lower temperatures. Iodine and sodium sulphate are valuable by-products. Chilean nitrate, in accordance with certain specifications, must contain a minimum of 95.5% of sodium nitrate, 1.5% of sodium chloride, 0.75% of potassium chloride, and 0.5% of borax. The nitrate shipped to markets carries approximately 16% of nitrogen, together with minor quantities of magnesium, iodine, boron, calcium, lithium, etc., desirable for plant growth.

Since their first commercial development in 1825 the Chilean deposits have yielded about 90 million tons of nitrate, the annual production during the past decade being about 1,400,000 tons, which is less than half the output of the peak years 1928-1929. In 1937 the combined nitrogen production of the world was obtained thus: 75% from air, 17% from coal, and 8% from Chilean nitrate. Nitratine is principally used as a fertiliser, and to a minor extent in the manufacture of chemical salts and explosives.

*References.*—R. B. Ladoo, "Non-Metallic Minerals," New York, 1925, 403-416; H. B. Graham, in "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, New York, 1937, Chap. XXXII (with short bibliography); G. A. Roush, "Strategic Mineral Supplies," New York, 1939, Chap. XIV; A. W. Allen, "The Recovery of Nitrate from Chilean Caliche," London, 1921; J. L. Rich, "Physiographic Setting of the Nitrate Deposits of Tarapacá, Chile; its bearing on the problem of origin and concentration," *Econ. Geol.* 1942, 37, 188.

D. W.

**NITRE** or **SALTPETRE**. A naturally-occurring potassium nitrate,  $\text{KNO}_3$ , crystallising in the orthorhombic system, usually as thin

white encrustations or as silky hair-like tufts. Hardness 2;  $\rho$  2.11. Readily fusible, giving violet flame, and easily soluble in water, with a saline and cooling taste. Nitre becomes rhombohedral at 339°C., but this modification does not occur as a natural mineral. The natural nitre commonly results from the action of bacteria on organic remains. About 10,000 tons of refined saltpetre are produced annually from saline efflorescences on the surface of the soil in Bihar, Central India, the deposits being formed by reaction between urine, cow-dung, and wood-ashes from domestic fires. It also occurs as delicate crusts on the surfaces of earth and rocks in arid regions, and in the soil of limestone caves. Potassium nitrate (saltpetre) is present to the extent of 2-3% in the sodium nitrate deposits of Chile, and a product usually referred to in the trade as nitrate of soda-potash, a mixture of sodium nitrate and potassium nitrate containing about 14% of nitrogen and 14% of  $\text{K}_2\text{O}$ , is exported mainly to the United States. Chile shipped more than 50,000 tons of soda-potash in 1940, chiefly for use as nitrogen-potash fertilizers. This Chilean nitrate is now finding increased competition from potassium nitrate prepared from crude potash salts. The refined nitrate finds service in curing meats, and in the manufacture of black powder, fireworks, and tobacco.

D. W.

**NITRILES** have the general formula  $\text{RC}\equiv\text{N}$  and can be regarded as esters of hydrocyanic acid. They can be hydrolysed to carboxylic acids without loss of carbon atoms and hence are often regarded not as esters of hydrocyanic acid but as derivatives of the acids which they yield on hydrolysis. Thus  $\text{CH}_3\cdot\text{CN}$  is called both methyl cyanide and acetonitrile.

Pelouze in 1834 obtained the first synthetic nitrile, propionitrile, by distilling barium ethyl sulphate with potassium cyanide.

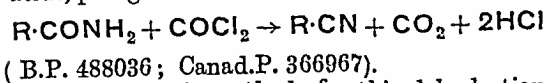
#### *Preparation.*

1. One of the most important methods consists in heating an organic halide (generally alkyl or arylalkyl) with potassium or sodium cyanide in alcohol. In place of the halide a salt of an alkyl sulphuric or phosphoric ester or an arylsulphonic ester can be used. The salts are heated with the cyanide without a solvent or in a non-aqueous solvent (U.S.P. 2298231). A small amount of isonitrile is usually formed when this method is used.

(2) By the dry distillation of amides or ammonium salts of organic acids with or without a dehydrating agent. This method has received many modifications and applications. A mixture of acid vapour and ammonia may be passed through a red hot tube (U.S.P. 2061314) or a mixture of acid and its ammonium salt may be heated together (B.P. 464106), alternatively ammonia may be passed through an acid or its ester and the resulting nitrile distilled off (F.P. 812369). Suitable dehydrating agents for the conversion of amides or ammonium salts into nitriles are phosphorus pentoxide, thionyl chloride, phosphorus trichloride or oxychloride in pyridine, dimethylaniline, *p*-toluenesulphonyl chloride (G.P. 512226; 485897; U.S.P. 1876652;



J. Indian Chem. Soc. 1941, 18, 164), acetic anhydride (B.P. 532938), benzotrichloride (G.P. 517760; 524715) or, for higher monobasic fatty acid amides and diamides of aromatic dibasic acids, phosgene can be used, *e.g.*,



Many catalytic methods for this dehydration have been described. Suitable catalysts are thorium, titanium oxide, boron phosphate, *bauxite*, *kaolin*, *silicates*, and various metals (B.P. 535187; 451594; G.P. 704494; F.P. 847296). Mixtures of alcohols, acids, acid chlorides, esters, and ammonia with catalysts give nitriles (Abe, J. Soc. Chem. Ind. Japan, 1933, 36, 42; Mailhe, *Compt. rend.* 1918, 166, 36, 121, 125; *idem*, *ibid.* 1920, 170, 813; *idem*, *Bull. Soc. chim.* 1918, [iv], 23, 380; *ibid.* 1920, [iv], 27, 266; Mitchell and Reid, J. Amer. Chem. Soc. 1931, 53, 321).

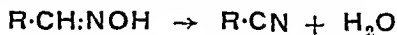
3. By diazotising a primary aromatic amine and decomposing the diazonium salt formed with cuprous cyanide or potassium cyanide and copper sulphate. An improved method involves decomposing the diazonium solution with alkali cupridiammonium cyanides or potassium cyanide and nickel chloride (B.P. 326149; G.P. 524187; U.S.P. 1879209; Korczynski and Fandrich, *Compt. rend.* 1926, 183, 421).

4. Hydrogen cyanide reacts with certain ethylenic compounds in the presence of basic catalysts to give nitriles, *e.g.*, with acrylic acid, and derivatives (G.P. 707852) or vinyl esters (G.P. 712373). Ammonia and a dehydration catalyst can replace hydrogen cyanide in this reaction (B.P. 295276; 332623; 332258; 326795; G.P. 467220; 526798; 528897; U.S.P. 1421743).

5. Alkyl isonitriles rearrange to nitriles on heating to 250°.

6. Nitriles are produced when cyanogen is passed into a boiling mixture of an aromatic hydrocarbon and aluminium chloride (Karrer and Zeller, *Helv. Chim. Acta*, 1919, 2, 482; Karrer, Rebmann, and Zeller, *ibid.* 1920, 3, 261).

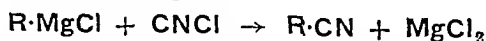
7. By dehydrating aldoximes,



with acetic anhydride or pyridine hydrochloride (Hauser and Vermillion, J. Amer. Chem. Soc. 1941, 63, 1224, 1227).

8. By heating an acid with a thiocyanate. Best results are obtained when the lead or zinc salt of the acid is heated with lead or cuprous thiocyanate or a mixture of lead ferrocyanide and sulphur (Reid, Amer. Chem. J. 1910, 43, 162; Van Epps and Reid, J. Amer. Chem. Soc. 1916, 38, 2120).

9. Nitriles are prepared, often in good yield, by the action of cyanogen or cyanogen chloride on a Grignard reagent.



(Grignard and Courtot, *Bull. Soc. chim.* 1915; [iv], 17, 228; Grignard and Ono, *ibid.* 1926, [iv], 39, 1589; Bellet and Courtot, *Ann. Chim.* 1920, [ix], 12, 364).

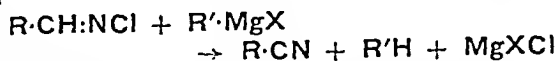
10. By treating cyanogen chloride with zinc alkyl.

11. By treating primary amines containing more than five carbon atoms with bromine and potassium hydroxide.

12. By removal of sulphur from isothiocyanates with metallic copper.

13. By heating diarylthioureas with zinc dust.

14. By the action of alcoholic potassium hydroxide, sodium ethoxide, or a Grignard reagent on an aldehyde chlorimine, *e.g.*,



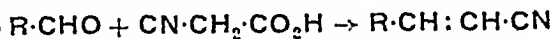
(Hauser and Gillespie, J. Amer. Chem. Soc. 1930, 52, 4517; Maistre, Rainsford, and Hauser, J. Org. Chem. 1939, 4, 106).

15. By distilling formamides with hydrochloric acid or zinc dust.

16. Dehydration of cyanohydrins with thionyl chloride, or catalytically, yields nitriles (G.P. 496372).

17. Certain amino-acids (*e.g.*, histidine, glycine, alanine) yield nitriles on treatment with sodium *p*-toluenesulphochloramide (Dakin, *Biochem. J.* 1916, 10, 319).

18. Unsaturated nitriles may be prepared by condensing cyanoacetic acid with aldehydes:



19. By passing the vapours of alkyl nitrites or amines over nickel at 300–400° (Sabatier and Gaudion, *Compt. rend.* 1917, 165, 224; Mailhe, *ibid.*, p. 557; 1918, 166, 996; *Bull. Soc. chim.* 1919, [iv], 25, 588).

### Properties.

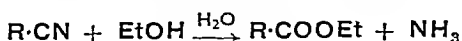
The lower nitriles are colourless liquids which can be distilled without decomposition. The higher members are crystalline solids.

	Formula.	M.p.	B.p.
Acetonitrile.	CH <sub>3</sub> ·CN	–41° to –44°	82°
Propionitrile	CH <sub>3</sub> ·CH <sub>2</sub> ·CN	–91·9°	97·1°
<i>n</i> -Butyronitrile.	CH <sub>3</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·CN	–112·6°	118°
Stearonitrile.	C <sub>17</sub> H <sub>35</sub> ·CN	+41°	274·5°/100 mm.
Benzonitrile.	C <sub>6</sub> H <sub>5</sub> ·CN	–13°	100·7°
Phenylacetoneitrile.	C <sub>6</sub> H <sub>5</sub> ·CH <sub>2</sub> ·CN	–23·8°	234°
Acrylonitrile	CH <sub>2</sub> :CH·CN	–82°	78–79°
Malononitrile	CH <sub>2</sub> (CN) <sub>2</sub>	+32·1°	220°

Excepting the lower members the nitriles are only slightly soluble in water. They are hydrolysed by acids and alkalis to ammonia and the corresponding carboxylic acid. Strong hydrochloric or sulphuric acid is usually required, and if these fail, alcoholic potassium hydroxide may be successful. Very resistant nitriles can often be hydrolysed with orthophosphoric acid (Berger and Olivier, *Rec. trav. chim.* 1927, 46, 600; Olivier, *ibid.* 1929, 48, 568), or the nitrile may be passed with steam over heated alumina or thorium (Mailhe, *Compt. rend.* 1920, 171, 245). By the action of alcoholic sulphuric or hydrochloric acid dinitriles are converted into esters

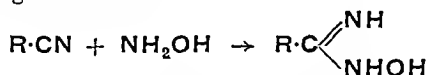


(Spiegel, Ber. 1918, 51, 216; Pfeiffer, *ibid.*, p. 805; Pfeiffer, Engelhardt, and Alfuss, Annalen, 1928, 467, 158).

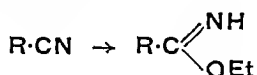


Usually the intermediate amides cannot be isolated when the simple nitriles are hydrolysed by the above method, but when heated with water at 180° or with alkaline hydrogen peroxide at 40°, acid amides are obtained (Radziszewski, Ber. 1885, 18, 355; Deinert, J. pr. Chem. 1895, [ii], 52, 431; McMaster and Langreck, J. Amer. Chem. Soc. 1917, 39, 103). Secondary amides are formed from nitriles by treating with organic acids, while treatment with acid anhydrides gives tertiary amides.

Hydroxylamine reacts with aliphatic nitriles giving amidoximes:

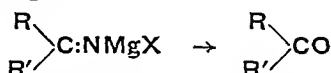


Hydrogen sulphide gives thioamides (Ralston, Van der Wal, and McCorkle, J. Org. Chem. 1939, 4, 68); an alcoholic solution of hydrogen chloride gives imino-esters:



(Pinner, Ber. 1883, 16, 353; 1884, 17, 184, 2002).

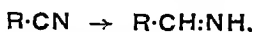
Grignard reagents react readily with nitriles, particularly aromatic nitriles, to give derivatives of ketimines from which ketones may be obtained by hydrolysis:



This is a useful method of preparation of ketones but cannot be used with the lower nitriles which polymerise under such conditions, or with nitriles containing reactive hydrogen atoms, e.g., cyanoacetic ester (Blaise, Compt. rend. 1901, 132, 839; 133, 1217; Bary, Bull. Soc. chim. 1922, [iv], 31, 397; Ectors, Bull. Soc. chim. Belg. 1924, 33, 146).

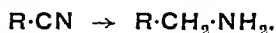
Ketones are also produced from nitriles by the Hoesch reaction (Ber. 1915, 48, 1112; 1917, 50, 462; Houben and Fischer, J. pr. Chem. 1929, [ii], 123, 89; *idem*, Ber. 1930, 63 [B], 2455, 2464), in which a phenol and the nitrile are condensed in the presence of hydrogen chloride sometimes together with zinc chloride. Polyhydric phenols undergo this reaction more readily than monohydric phenols.

When a nitrile is added to a mixture of stannous chloride and ethereal hydrochloric acid reduction takes place and an aldimine is formed,



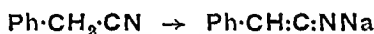
which is hydrolysed rapidly with warm water to the corresponding aldehyde (Stephen, J.C.S.

1925, 127, 1874; 1930, 2786; King, L'Ecuyer, and Openshaw, *ibid.* 1936, 352). More vigorous reduction with sodium and ethyl or amyl alcohol gives an amine:

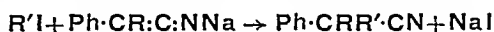
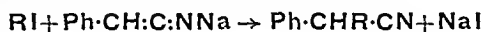


It is more usual to carry out this reduction catalytically with hydrogen. In neutral solution a mixture of primary and secondary amines results (von Braun, Blessing, and Zobel, Ber. 1923, 56 [B], 1988; Winans and Adkins, J. Amer. Chem. Soc. 1932, 54, 306). The use of a platinum catalyst and glacial acetic acid as solvent increases the yield of primary amines (Kindler, Peschke, and Dehn, Annalen, 1931, 485, 113; Rosenmunde and Pfannkuch, Ber. 1923, 56 [B], 2258). Good yields of acetylated primary amines have been obtained when reduction was carried out in acetic anhydride using a platinum catalyst (Carothers and Jones, J. Amer. Chem. Soc. 1925, 47, 3051; Schales, Ber. 1935, 68 [B], 1943). Primary amines are also formed by reduction of nitriles with palladium-charcoal in alcoholic hydrogen chloride (Hartung, J. Amer. Chem. Soc. 1928, 50, 3370) or with nickel in the presence of ammonia at 100–150° (Winans and Adkins, *l.c.*; Schwoegler and Adkins, *ibid.* 1939, 61, 3499; U.S.P. 2166151).

Metallio derivatives can be obtained from nitriles which contain a hydrogen atom on the carbon atom which carries the cyanide group, e.g., phenylacetonitrile forms a sodio or potassio derivative when treated with the metal in an inert solvent in an atmosphere of nitrogen (Upson, Maxwell, and Parmelee, J. Amer. Chem. Soc. 1930, 52, 1971; Rising and Lowe, *ibid.* p. 2524):

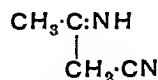


the hydrogen liberated during the reaction reduces some of the derivative to toluene and sodium cyanide. In liquid ammonia the sodio derivative of phenylacetonitrile is formed exclusively (Baldinger and Nieuwland, *ibid.* 1932, 54, 828; 1933, 55, 2851). The metallic derivatives are inflammable in air, phenylsodioacetonitrile giving benzoic acid and sodium cyanide; on heating this derivative stilbene is formed. Alkyl halides react readily with these derivatives giving secondary or tertiary nitriles:

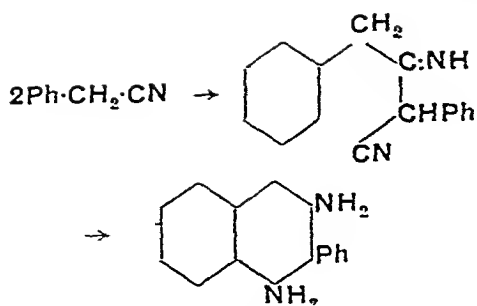


(Baldinger and Nieuwland, *l.c.*; Ramart, Compt. rend. 1926, 182, 1226; B.P. 253950; F.P. 728241; G.P. 473329; U.S.P. 1690325).

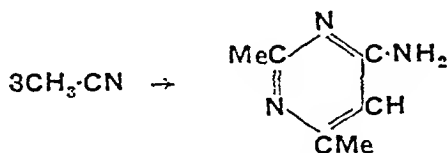
Under certain conditions nitriles polymerise readily. On treating with sodium or sodamide in ether, bimolecular products are obtained, e.g., acetonitrile gives the imino-nitrile of acetoacetic acid:



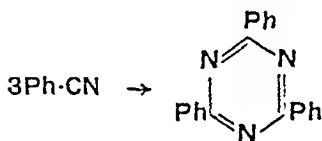
Phenylacetonitrile under similar conditions gives first a dimer which ring-closes:



This reaction has been studied extensively by J. F. Thorpe (*cf.* Atkinson and Thorpe, J.C.S. 1906, 89, 1906; 1907, 91, 578; 1909, 95, 1901) and has found many useful applications in the synthesis of organic compounds. Under more vigorous conditions nitriles of the type of acetonitrile and phenylacetonitrile give trimolecular products, *e.g.*, acetonitrile on heating with sodium ethoxide gives a pyrimidine, cyanomethine:



in a similar manner purely aromatic nitriles, *e.g.*, benzonitrile, give triazines:



#### Detection of Nitriles.

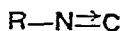
Nitriles can be detected by reduction to the corresponding amines with sodium and alcohol and these identified by the usual methods; hydrolysis to amides has also been used (Cutter and Taras, *Ind. Eng. Chem. [Anal.]*, 1941, 13, 830; Rovira and Palfray, *Compt. rend.* 1940, 211, 396). Treatment of nitriles with Grignard reagents to give ketones which form characteristic derivatives has been described as a method of identification (Schriner and Turner, *J. Amer. Chem. Soc.* 1930, 52, 1267). Condensation with phloroglucinol (Houben-Hoesch synthesis) gives readily characterised phlorophenones (Howells and Glenn, *ibid.* 1932, 54, 2451).

#### isoNitriles.

isoNitriles, isocyanides, or carbylamines have the general formula:



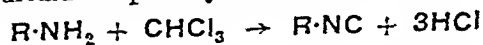
(Nef, *Annalen*, 1892, 270, 267; 1895, 287, 265), or:



(Langmuir, *J. Amer. Chem. Soc.* 1919, 41, 1543; Hammick, New, Sidgwick, and Sutton, *J.C.S.* 1930, 1876).

The first isonitriles were prepared in 1866 by Gautier by the action of silver cyanide on alkyl

iodides. Later Hofmann prepared them by the action of chloroform and alcoholic potassium hydroxide on primary amines:



They are formed during the preparation of nitriles (*see* Method 1) and when sodium hypochlorite reacts with certain ureides in alkaline solution (Dumont and Declercq, *J. Pharm. Belg.*, 1931, 13, 925).

The isonitriles are reactive, volatile liquids with an extremely repulsive odour. Their formation is often used as a method for the detection of primary amines.

	Formula.	B.p.
Methyl isocyanide . . .	$\text{CH}_3\cdot\text{NC}$	59°
Ethyl isocyanide . . .	$\text{CH}_3\cdot\text{CH}_2\cdot\text{NC}$	78°
Phenyl isocyanide . . .	$\text{C}_6\text{H}_5\cdot\text{NC}$	166°

They are sparingly soluble in water and decompose on heating or standing for some time. They are stable to alkalis but are hydrolysed very readily with dilute acids or water at 180° giving formic acid and primary amines. With hydrochloric acid in ether, isonitriles, although not basic, form compounds of the type:



With sulphur above 100° they give mustard oils, isothiocyanates:



With hydrogen sulphide thioformamides are produced, while with mercuric oxide isocyanates result:



On reduction with sodium in amyl alcohol or catalytically, secondary amines are produced containing one methyl group:



For a review of the reactions of isonitriles, *see* Passerini, *Atti R. Accad. Lincei*, 1927, [vi], 2, 377.

J. B.

**NITROANILINES.** *Ortho*- and *para*-nitroanilines are prepared by two methods, the nitration of aniline derivatives and the amination of the corresponding chlorobenzenes. Nitration of aniline in sulphuric acid at -20° yields far less *ortho*- than *para*-isomer, which is, however, accompanied by an almost equal quantity of *meta*- owing to the large amount of aniline sulphate formed. Nitration of acetanilide similarly gives mainly the *para*-isomer, the amount of *ortho*- varying considerably with the conditions, being increased especially by the use of acetyl nitrate as reagent (Pictet, *Ber.* 1907, 40, 1165). Full details of the proportions of the different products obtained under varying conditions in all these cases are given by Hollemann, Hartogs, and Van Linden (*ibid.* 1911, 44, 704). Müller (*Chem.-Ztg.* 1912, 36, 1055) describes the technical preparation of *p*-nitroaniline from aniline via acetanilide on the 200 kg. scale. The device of blocking the *para*-position by sulphonation affords a similar route to

*o*-nitroaniline. Sulphonation of oxanilide, followed by nitration, gives 2:2'-dinitro-oxanilide-4:4'-disulphonic acid, which is desulphonated by hot acid (Wülfing, G.P. 65212; 66060). The hydrolysis of technical 2-nitroaniline-4-sulphonic acid by hot sulphuric acid is a convenient laboratory method (Ehrenfeld and Puterbaugh, "Organic Syntheses," 9, 64; Sakellarios and Jatrides, Ber. 1925, 58 [B], 2286).

The amination of nitrochlorobenzenes is the subject of numerous patents. Details for the *para*-compound are given by the Clayton Aniline Co. (G.P. 148749), by Vasserman (J. Chem. Ind. Russ. 1930, 7, 1523), and in a series of patents by Saunders (B.P. 329260; 336136; U.S.P. 1911717). It is claimed that the reaction is improved by the addition of lead dioxide and sodium acetate (Frye, U.S.P. 2104983), and salts of bivalent copper (Vorozhtzov and Kruilova, J. Gen. Chem. Russ. 1934, 4, 324). Corrosion of plant is reduced by the presence of amines (Dupont, B.P. 439055). Autoclaving with ammonia may be avoided by simple heating with ammonium acetate (Soc. Chim. de la Grande-Paroisse, G.P. 376796).

The removal of *o*-nitroaniline from the crude *para*-compound is accomplished by treatment with hot alkali (Merrill, U.S.P. 1692308; 1786766; Davis, U.S.P. 1903030; Frye, U.S.P. 2128699; Vorozhtzov and Kozlov, J. Gen. Chem. Russ. 1939, 9, 587) or reducing agents (Miller, U.S.P. 1673154; 1848137). The best method of laboratory purification of *o*-nitroaniline is that of Kuhn and Ströbele (Ber. 1937, 70 [B], 779) by chromatography on alumina in benzene.

Methods of analysis of such mixtures are by setting-points (Holleman, Hartogs, and Van Linden, *ibid.* 1911, 44, 704) and chromatography on calcium hydroxide (Karrer and Neilsen, Ber. Ges. Physiol. Exptl. Pharmakol. 86, 529; Amer. Chem. Abstr. 1937, 31, 6531). Specific techniques for determination of *ortho*- and *para*-compounds in the *meta*- are by estimation of the ammonia evolved by alkali (Semiganowski, Z. anal. Chem. 1927, 72, 27) and bromination (Shiviskaya, Prom. Org. Chim. 1936, 1, 163). Steam distillation (Terent'ev, Klimova, and Puziureva, Amer. Chem. Abstr. 1935, 29, 2479), and reduction followed by colorimetric estimation with acetylacetone (Kulikov and Panova, J. Gen. Chem. Russ. 1932, 2, 736) serve for *ortho*- in *para*-. The *para*-isomer in the *ortho*- may be estimated by conversion to the phenols, steam distillation, and titration of the residue after reduction to *p*-aminophenol (Sheherbachev, Prom. Org. Chim. 1938, 5, 753).

*o*-Nitroaniline.—Manufacture and preparation as above. Golden yellow plates or needles from water, m.p. 71.5°, soluble in hot water and organic solvents.

*m*-Nitroaniline is prepared by the reduction of *m*-dinitrobenzene, usually by sodium sulphide (typical procedure—Cobenzl, Chem.-Ztg. 1913, 39, 799). More recent modifications include the addition of ammonium chloride (Kirchov and Eskin, Amer. Chem. Abstr. 1930, 25, 2441), sodium bicarbonate (Vorontzov, J. Chem. Ind. Russ. 1930, 7, 2145), and an inert solvent such as naphtha. Alternative reducing

agents are manganous sulphide (Dawes, U.S.P. 1765660), iron turnings and chloride (Lyons and Smith, Ber. 1927, 60 [B], 719; Laubashevich and Voroshilova, Prom. Org. Chim. 1937, 4, 253). Yellow needles from water, m.p. 114°, soluble in hot water and organic solvents.

*p*-Nitroaniline.—Manufacture and preparation as above. Pale yellow needles from water, m.p. 148°, soluble in hot water and organic solvents, not volatile in steam.

2:4-Dinitroaniline may be manufactured from 2:4-dinitrochlorobenzene by treatment with ammonia under pressure. Heating with ammonium acetate is more convenient (Soc. Chim. de la Grande-Paroisse, G.P. 376796), especially in the laboratory (Wells and Allen, "Organic Syntheses," 15, 22); an alternative is urea (Päster, U.S.P. 1752998). It forms yellow needles from aqueous acetone, m.p. 180°, sparingly soluble in cold alcohol and hot water. It is feebly basic and is readily converted by alkali to the corresponding phenol.

The remaining dinitroanilines may be prepared according to the procedures used by Welsh (J. Amer. Chem. Soc. 1941, 63, 3276).

2:4:6-Trinitroaniline, *Picramide*. Hollemann (Rec. trav. chim. 1930, 49, 112) gives details of the preparation from *p*-nitroaniline, and from acetanilide.

2:3:4:6-Tetranitroaniline has been suggested as an explosive (T.N.A.) (v. Vol. IV, 487*d*) by Flürscheim, who gives a comprehensive review of the subject (J.S.C.I. 1921, 40, 97*r*). Macciotta (Gazzetta, 1930, 60, 408) describes the preparation of the corresponding nitroamine, which is decomposed to the aniline acid.

G. W. K.

**NITROCALCITE.** A mineral consisting of hydrated calcium nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ , probably identical with the artificial monoclinic salt  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  ( $\rho$  1.90). It occurs as an efflorescence of white silky fibres, and is usually found in limestone caves in association with nitre (*see* p. 484*b*). It is sometimes seen as an efflorescence on the walls of stables ("wall-saltpetre"). Calcium nitrate is now manufactured on a large scale from atmospheric nitrogen for use as a fertiliser (v. CALCIUM, Vol. II, 203*d*).

L. J. S.

**NITROCELLULOSES** (v. Vol. IV, 501-535).

**NITROCHALK** (v. Vol. I, 352*d*; V, 65*c*).

**NITRO-COMPOUNDS, ALIPHATIC.**

The first nitroparaffin was made by Victor Meyer in 1872, by the interaction of amyl iodide with silver nitrite. Some interest was aroused at that time on account of the great chemical reactivity of this series but not until recent years has the method of direct nitration of the paraffins in the vapour phase rendered the lower members (from nitromethane to nitrobutane) available in quantity and opened up the possibilities of their technical exploitation. In this article it is proposed to review the general chemistry of aliphatic nitro-compounds under the three headings: I, Mononitroparaffins and their derivatives; II, Polynitro-compounds; and III,  $\Delta^4$ -Nitro-olefins and their derivatives.

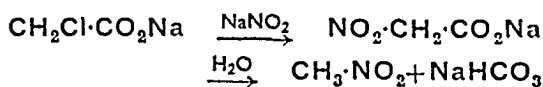
A final section, IV, deals with their known and potential uses. In view of the new extensive literature of this subject it is impossible to give a full bibliography in a short article; where literature references are quoted, therefore, the most relevant have been chosen as far as possible.

### I. MONONITRO-COMPOUNDS AND THEIR DERIVATIVES.

#### Preparation.

(a) *By Interaction between Metallic Nitrites and Halogen or Sulphate Esters of Alcohols.*—A nitropentane was first prepared by Victor Meyer (Ber. 1872, 5, 203) by heating amyl iodide with silver nitrite. The method is a general one and yields a mixture of the nitro-paraffin and the corresponding alkyl nitrite in relative amounts which vary with the nature of both the halogen and alkyl group (Reynolds and Adkins, J. Amer. Chem. Soc. 1929, 51, 279), and which are readily separated owing to their widely different boiling-points. This method has been extended to the preparation of nitro-olefins other than  $\Delta^2$ , nitro-ketones, nitro-acids, and nitro-esters. Silver may be replaced by mercury, and the use of sodium nitrite in the preparation of nitromethane from methyl chloride or bromide has been described (Great Western Electro-Chemical Co., U.S.P. 2105581; 2117931). A further variation is the use of alkali or alkaline earth nitrites with dimethyl or diethyl sulphates or salts of the corresponding hydrogen sulphates (cf. McCombie, Saunders, and Wild, J.C.S. 1944, 24).

Salts of  $\alpha$ -halogenated carboxylic acids in which the halogen is attached to a primary or secondary carbon atom react with alkali nitrites to give salts of  $\alpha$ -nitrocarboxylic acids which are readily decomposed to the corresponding nitroparaffin. Thus, nitromethane is obtained in 51% yield from chloroacetic acid (Organic Syntheses, Coll. Vol. I, 393):



This is the only case in which a good yield is quoted.

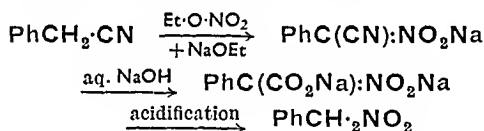
(b) *Liquid-phase Nitration.*—Although the paraffins are not nitrated as readily as are olefins and aromatic hydrocarbons, nitro-paraffins have been obtained from hydrocarbons, ranging from the pentanes to the residues from the distillation of petroleum, by treatment with hot nitric acid (Ellis, Chemistry of Petroleum Derivatives, Chemical Catalog Co. Inc., New York, I, 1040; Reinhold Publishing Corp., New York, II, 1090). Paraffins or cyclo-paraffins containing a tertiary carbon atom yield tertiary nitroparaffins. In the absence of a tertiary carbon atom, although the entering nitro-group attaches itself to a secondary (usually in the 2 position), rather than to a primary carbon atom, primary nitro-compounds are also formed in small amounts. The reaction is slow owing to the mutual insolubility of the reagents. Moreover, due to the solubility of the initially formed nitro-compound in the nitric acid, by-products such as polynitro-compounds

and oxidation and hydrolysis products are also produced. As a consequence, the yield of mononitro derivatives is often poor. Increase in temperature results in more rapid reaction and better yields, and a 60% yield of 2-nitro-hexane has been obtained from *n*-hexane by use of dilute nitric acid at a relatively high temperature (140°) in a sealed tube; hot dilute nitric acid also nitrates the side chains of aliphatic compounds (e.g., toluene) without nitration of the nucleus. In the case of the higher paraffins ( $\text{C}_8$ – $\text{C}_{18}$ ), superheated nitric acid vapour may be passed through the hydrocarbon at 121–200°. According to Grundmann (Die Chemie, 1943, 56, 159, 323) reaction then gives all the *sec.*-nitro-compounds to be expected from random nitration. Nitric-acetic acid mixtures, benzoyl nitrate, and acetyl nitrate have also been used, but all suffer from the disadvantage that they are not stable under the reaction conditions. Sulphuric-nitric acid mixtures are unsuitable since primary nitroparaffins are quickly hydrolysed by hot sulphuric acid, while secondary and tertiary nitro-compounds are converted into tars. Little is known about the mechanism of these nitrations except that free radicals are not involved (Stevens and Schiessler, J. Amer. Chem. Soc. 1940, 62, 2885). The introduction of negative groups into paraffins facilitates nitration. Thus, Konowaloff found that chloro derivatives of butane and pentane were more easily nitrated than the hydrocarbons themselves (Chem. Zentr. 1904, 75, I, 1478; II, 200; 1906, 77, II, 1552), while both ethyl acetate and acetoacetic ester give nitroacetic ester with fuming nitric acid in acetic anhydride at 30–35° [Boucault and Wahl, Bull. Soc. chim. 1904, [iii], 31, 847]. Malonic ester and its amide are nitrated even more readily (Menke, Rec. trav. chim. 1930, 49, 381).

(c) *Vapour-phase Nitration.*—More recently, H. B. Hass and his collaborators (Ind. Eng. Chem. 1936, 28, 339; 1938, 30, 67; 1939, 31, 648; 1940, 32, 427; 1941, 33, 1138; 1942, 34, 300) have developed a new method for the nitration of paraffins which depends upon operation in the vapour phase. The gaseous paraffins were nitrated for the first time by this means. Methane is less easily nitrated than the higher paraffins. Ethane is nitrated somewhat more easily but not as readily as propane; no appreciable difference has been observed in the case of paraffins higher than propane. Although paraffins as high as undecane have thus been nitrated the liquid-phase method described by Grundman (*loc.*) is probably more suitable for the less volatile hydrocarbons since the higher nitroparaffins from  $\text{C}_8\text{H}_{17}\cdot\text{NO}_2$  begin to decompose at their boiling-points. Nitrogen peroxide may be used to replace nitric acid (I.C.I., B.P. 527031; Hass and Riley, Chem. Reviews, 1943, 32, 381). Increase in temperature or pressure increases the speed of the reaction. At low temperatures (100–200°) tertiary paraffins give tertiary nitro-compounds, while in other cases the entering nitro-group attaches itself to a secondary carbon atom rather than to a primary, as in the case of liquid-phase nitration (Hass and Riley, *loc.*; Hass, Ind. Eng. Chem. 1943, 35,

1146; I.C.I., *l.c.*). Dinitro-compounds are also formed. At higher temperatures (248–600°) the speed of the reaction is greatly increased, so that a continuous flow process can be conveniently employed, but the character of the product is entirely changed. A mixture of all the mononitro-compounds which could theoretically result by replacing either any hydrogen atom or any alkyl radical in the hydrocarbon molecule with a nitro-group is obtained. Polynitroparaffins are not formed unless paraffins of rather high molecular weight are used, but a considerable amount of oxidation accompanies the reaction. In contrast to the liquid-phase method, however, very little of the nitrating agent is degraded to elementary nitrogen. The Commercial Solvents Corporation have erected a pilot plant at Peoria, Illinois, for the nitration of propane, *n*-butane, and isobutane by the high temperature continuous flow process, and in May 1940 began the nitration of propane; they now market nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane; 1- and 2-nitrobutane have also been supplied in small lots. The mechanism of the reaction is obscure and is still under active investigation. Although cycloparaffins and chloroparaffins have also been nitrated in the vapour phase, very few other aliphatic compounds have been treated in this manner (*cf.* Hass and Riley, *l.c.*).

(*d*) *Miscellaneous*.—A nitro-group may be introduced into a compound containing reactive methylene (*e.g.*, benzyl cyanide, cyclopentadiene) by condensation with ethyl nitrate in the presence of sodium ethoxide. Phenylnitromethane is most conveniently prepared by this method (*Organic Syntheses*, 19, 73):



1:2-Nitrochloro-compounds have recently been obtained by the addition of nitryl chloride to olefins (Steinkopf and Küknel, *Ber.* 1942, 75 [B], 1323).

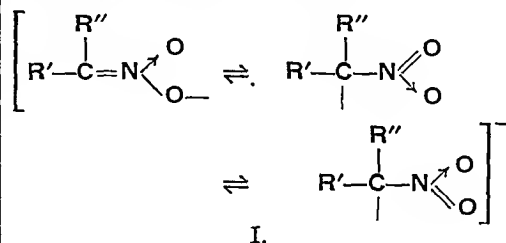
### Physical Properties.

The mononitroparaffins ( $\text{C}_1\text{--C}_{18}$ ) are colourless liquids possessing boiling-points considerably higher than the parent hydrocarbon, and high dielectric constants. They are sparingly soluble in water, the solubility decreasing as the series is extended, but are soluble in the majority of organic solvents. The lowest member of the series, nitromethane, is anomalous in not being miscible with paraffins, and its use as a selective solvent in petroleum refining has been proposed (*see p.* 497*b*). Their toxicity is of a low order (about the same as petroleum naphtha).

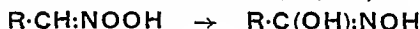
### Reactions.

(*a*) *Action of Acids and Bases*.—Primary and secondary nitroparaffins dissolve in aqueous or aqueous-alcoholic solutions of strong alkalis to form salts: tertiary ones do not. This is due to the fact that the first two can exist in two tautomeric forms, the normal and the salt-

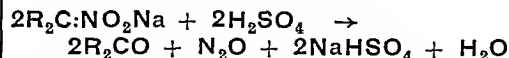
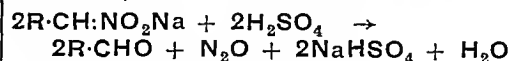
forming *iso*- or *aci*-form (also known as nitronic acids). Most of the chemistry of the aliphatic nitro-compounds arises from the reactivity of the *aci*-forms. They are apparently weaker acids than carbonic, since nitroparaffins can be regenerated from their salts by treatment with carbon dioxide. The structure of their salts is still unsettled (Hass and Riley, *l.c.*), but their properties suggest the presence of the hybrid



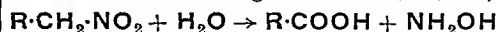
anion (I) in which the first structure predominates. Thus, optically active sodium salts are known to exist and both C and O derivatives have been obtained on alkylation or acetylation. When these salts are acidified, the *aci*-form is released and in some cases, particularly when it is solid, can be isolated. The free acid form may then isomerise to the nitro-form on standing. To isolate the *aci*-form or the corresponding nitro-compound the acidification is best carried out either at a very low temperature or with a weak acid such as carbon dioxide or acetic acid; otherwise at room temperature, if the *aci*-form is derived from a primary nitro-compound, rearrangement to a hydroxamic acid may occur (*cf.* Yale, *Chem. Reviews*, 1943, 33, 226):



or it may decompose to nitrous oxide and an aldehyde (or a ketone in the case of a secondary derivative). In many cases the latter reaction predominates when an aqueous solution of the salt is added to excess cold dilute sulphuric acid, and aldehydes (or ketones) are obtained in 85% yield (Johnson and Degering, *J. Org. Chem.* 1943, 8, 10).

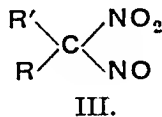
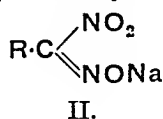


Aldehydes and ketones may also be obtained in excellent yield by oxidation of the salts of primary and secondary nitro-compounds respectively with potassium permanganate or hydrogen peroxide (Nametkin and Posdnjakowa, *Chem. Zentr.* 1914, I, 757). On the other hand, if the acidification of a salt derived from a primary nitro-compound is carried out with hot acid, carboxylic acids are obtained by hydrolysis of the hydroxamic acid shown above. Excellent yields of carboxylic acids and hydroxylamine can also be obtained by heating the primary nitroparaffins with 85% sulphuric acid (Lippincott and Hass, *Ind. Eng. Chem.* 1939, 31, 118):



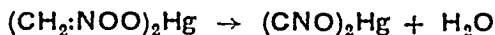
Secondary nitroparaffins yield tars with hot mineral acids.

Primary, secondary, and tertiary aliphatic nitro-compounds can be differentiated from one another by reaction with nitrous acid in alkaline solution. The primary compounds give a red coloration due to the formation of a nitrelic acid salt (II), while the secondary derivatives give a blue colour due to the formation of a  $\psi$ -nitrolo (III). Tertiary derivatives do not react.

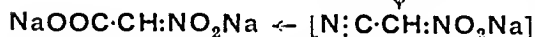
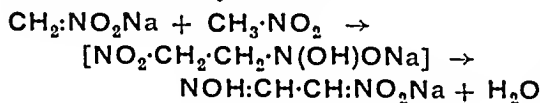


$\psi$ -Nitroles are converted into the corresponding dinitro-compounds on oxidation with chromic acid, whilst with hydroxylamine or sodium amalgam in alkaline solution they yield ketoximes.

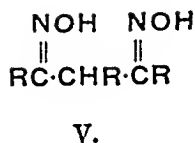
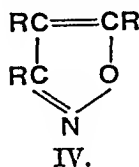
The sodium salts of the aliphatic nitro-compounds are usually colourless crystalline solids (cf. Hantzsch, Ber. 1907, 40, 1523) soluble in water but sparingly soluble in alcohol. When crystallised from alcohol they often contain alcohol of crystallisation and when dry are unstable. For example, sodium nitromethane explodes on heating on a water bath, on treatment with a little water, or on subjection to a sharp blow. The potassium salt is unstable at room temperature. Sodium nitroethane also explodes on heating gently. Aqueous solutions of these salts can often be precipitated by the salts of heavy metals. Sodium nitromethane is exceptional in that it gives with mercuric chloride a 20% yield of mercuric fulminate by loss of water from the initially formed mercuric salt.



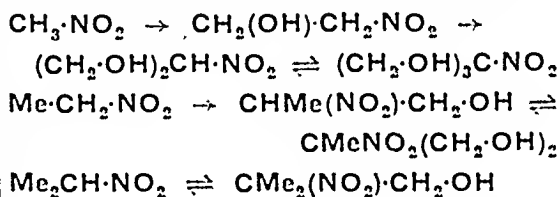
When nitromethane is heated with strong alkalis, salts of methazonic acid, and nitroacetic acid are successively formed:



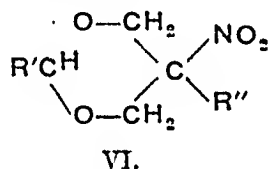
The intermediate nitroacetonitrile can be obtained by action of ethereal thionyl chloride on methazonic acid (Steinkopf and Bohrmann, *ibid.* 1908, 41, 1048). The higher primary nitroparaffins also undergo self-condensation on treatment with alkalis, but in this case three molecules take part. With inorganic bases, trialkylisooxazoles (IV) are obtained, whilst organic bases yield 1:3-dioximes (V) which, it is suggested, are intermediates in the former reaction (Lippincott, J. Amer. Chem. Soc. 1940, 62, 2604).



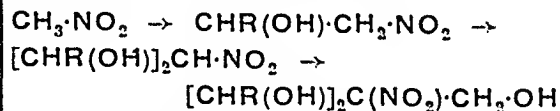
(b) *Condensation with Aldehydes.*—Almost all primary and secondary nitro-compounds condense with aldehydes in the presence of a catalyst. Basic catalysts (either inorganic or organic) are most commonly used but zinc chloride has been employed with aromatic aldehydes. In the case of formaldehyde, one or more of the  $\alpha$ -hydrogen atoms is replaced by a methylol group according to the reaction conditions and when the product contains no free  $\alpha$ -hydrogen, the process can be partially reversed, i.e., one methylol group can be removed, usually by treatment with one molecule of strong alkali:



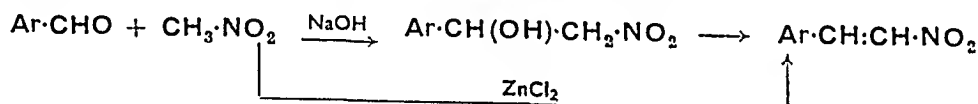
Cyclic acetals of type (VI) have been prepared from several of these diols and triols by further condensation with aliphatic aldehydes (Senkus, *ibid.* 1941, 63, 2635).



Higher aliphatic aldehydes yield alcohols in a similar manner, but here condensation is more difficult when only one  $\alpha$ -hydrogen atom is present; the last hydrogen atom, however, is readily replaced by a methylol group as described above:



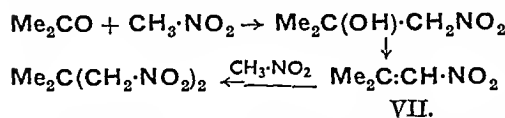
With basic catalysts, aromatic aldehydes yield monohydric alcohols but special precautions must be taken if it is desired to isolate them, since nitro-alcohols of these types are very readily dehydrated. Using zinc chloride as catalyst unsaturated nitro-compounds are obtained directly:



The nitro-alcohols can be esterified by the usual methods to give acetates, phthalates, phosphates, and similar compounds. The trinitrate of trimethylol nitromethane is stated to have excellent explosive properties similar to

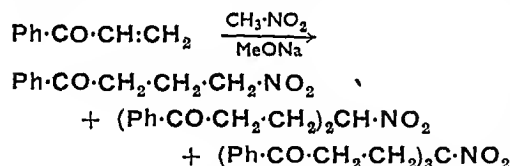
nitroglycerine, but to be more stable and to have a lower freezing-point (Hofwinmer, J.S.C.I. 1912, 31, 204). Certain nitro-alcohols have been oxidised to the corresponding nitro-ketones (Parkes and Williams, J.C.S. 1934, 67).

(c) *Condensation with Ketones.*—Nitromethane reacts with ketones such as acetone, methyl ethyl ketone, diethyl ketone, and methyl propyl ketone under the influence of a basic catalyst to give 1:3-dinitroparaffins (Fraser and Kon, *ibid.* 1934, 604). Since 1-nitro-2-methyl propene (VII) has been isolated from the product of the reaction between acetone and nitromethane and shown to react with nitromethane (Hass, *Ind. Eng. Chem.* 1943, 35, 1150) this reaction is believed to occur in the following manner:

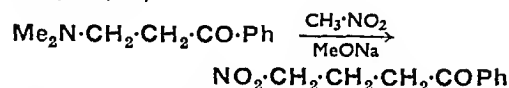


*cyclo*Hexanone and *cyclopentanone* behave similarly with the formation of nitro-alcohols. Isatin,  $\alpha$ -diketones, and phenathraquinone also yield nitro-alcohols on condensation with primary nitroparaffins (Zrike and Lindwall, *J. Amer. Chem. Soc.* 1935, 57, 207; Jakubowitsch, *J. pr. Chem.* 1935, [ii], 142, 37; Fujise *et al.*, *Ber.* 1935, 68 [B], 1272).

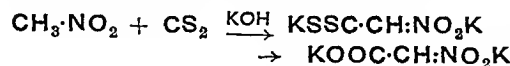
(d) *Addition to Double Bonds.*—Under the influence of a basic catalyst, many primary and secondary aliphatic nitro-compounds will condense with compounds containing an activated double bond. The reaction takes place most readily with  $\alpha\beta$ -unsaturated ketones; and when the initial product is a primary or secondary nitro-compound, further reaction may occur, e.g.,



$\alpha\beta$ -Unsaturated esters, nitriles, and nitro-compounds and benzylideneaniline have also been employed. It is interesting to note that Mannich bases derived from methyl ketones react with sodium nitromethane to form similar products (Reichert and Posemann, *Arch. Pharm.* 1937, 275, 67):



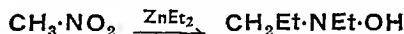
Nitromethane also condenses with carbon disulphide in the presence of alcoholic potassium hydroxide; further treatment of the resulting dithioacid salt with hot aqueous alkali yields the corresponding salt of nitroacetic acid,



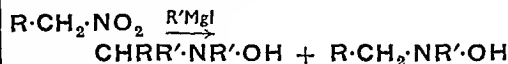
Nitromethane and phenyl isocyanate yield  $\omega$ -nitroacetanilide,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , and nitromalonanilide,  $\text{NO}_2\cdot\text{CH}(\text{CO}\cdot\text{NHPh})_2$ , under suitable conditions.

(e) *Reduction.*—Aliphatic nitro-compounds have been reduced to amines by a large variety of reducing agents, but the best yields result from the use of either iron and acetic acid or Raney

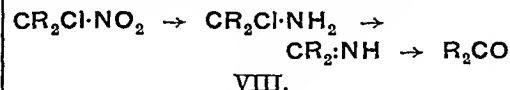
nickel and hydrogen under pressure. Weak neutral reducing agents such as zinc dust and water or aluminium amalgam yield hydroxylamines, also obtained in poor yield using sodium in liquid ammonia (Watt and Knowles, *J. Org. Chem.* 1943, 8, 540), and in many cases in good yield by electrolytic reduction in the cold (Bruckner, Kramli, and Vinkler, *Amer. Chem. Abstr.* 1939, 33, 1602). Catalytic methods ( $\text{Pd}/\text{H}_2$  in the presence of oxalic acid) have been used for the preparation of hydroxylamines from certain nitro-alcohols (Wilkendorf and Trenel, *Ber.* 1923, 56 [B], 611). Primary and secondary nitro-paraffins yield  $\beta$ -dialkylhydroxylamines on treatment with zinc dialkyls (Bewad, *Chem. Zentr.* 1900, II, 942; *J. pr. Chem.* 1901, [ii], 63, 193; Mamlock and Wolfenstein, *Ber.* 1901, 34, 2503). Thus, N-ethyl-N-propylhydroxylamine is obtained from nitromethane and zinc diethyl:



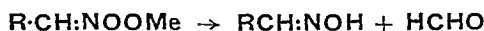
Alkyl zinc iodides behave similarly, but Grignard reagents give a mixture of two  $\beta$ -dialkylhydroxylamines (Bewad, *ibid.* 1907, 40, 3065; Moureu, *Compt. rend.* 1901, 132, 838; Wang, *Trans. Sci. Soc. China*, 1933, 7, 253):



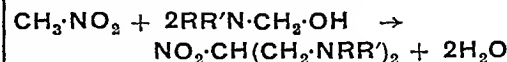
Sodium amalgam or zinc dust in alkaline solution converts many primary and secondary nitro-compounds into oximes, which are also obtained in excellent yield when a solution of the sodium salt of the nitro-compound is treated with stannous chloride and hydrochloric acid in the cold (Konowaloff, *Chem. Zentr.* 1899, I, 597). Reduction of primary and secondary nitroparaffins with zinc dust and glacial acetic acid, followed by hydrolysis of the resulting oximes *in situ* has given the corresponding aldehydes and ketones in 43% yield (Johnson and Degering, *J. Amer. Chem. Soc.* 1939, 61, 3194). Tertiary nitroparaffins do not give oximes, but chloro-compounds of type (VIII) have been reduced by catalytic means to ketones.



Oximes can also be obtained by the decomposition of the methyl esters of the nitronic acids (Arndt and Rose, *J.C.S.* 1935, 1):



(f) *Condensation with N-Methylolamines.*—Interaction of nitromethane with N-methylol-derivatives of *sec*-aliphatic and heterocyclic amines leads to replacement of two hydrogen atoms and formation of a derivative of 2-nitro-1:3-propylenediamine:

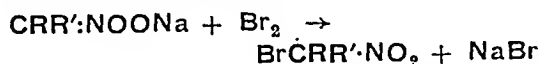


With the higher nitroparaffins a similar reaction may lead to replacement of either or both of the reactive hydrogen atoms (*cf.* De Mauny, *Bull. Soc. chim.* 1937, [v], 4, 1451, 1460). The re-



action is presumably reversible, as treatment of 2-nitro-1:3-di(dimethylamino)-propane with aniline gives 2-nitro-1:3-dianilino-propane by displacement of dimethylamine (Dudcn, Bock, and Reid, Ber. 1905, 38, 2036).

(g) *Halogenation*.—The *aci*-form and alkali salts of primary and secondary nitroparaffins react with halogens with great ease to give  $\alpha$ -halogen derivatives

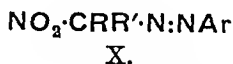
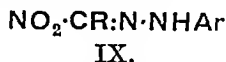


All  $\alpha$ -hydrogen atoms in nitroparaffins may thus be replaced, but to obtain the polyhalogenonitromethanes, the presence of strong alkali must be avoided. Thus, chloropicrin is prepared by treatment of nitromethane with an alkali hypochlorite or with chlorine in the presence of calcium carbonate (Great Western Electro-Chemical Co., U.S.P. 1996388; Commercial Solvents Corp., U.S.P. 2181411; cf. Jackson, Chem. Reviews, 1934, 14, 251).  $\alpha$ -Chloro- and  $\alpha$ -bromo-nitroparaffins are more stable than the corresponding iodo-compounds, many of which decompose on distillation (Soiglo and Hass, J. Org. Chem. 1940, 5, 100). Little is known about the reactivity of the halogen in these derivatives although certain members yield higher nitroparaffins with zinc dialkyls (Bewad, Ber. 1891, 24, 973; 1893, 26, 129), and with the sodium salts of *sec*-nitroparaffins give 1:2-dinitroparaffins (Soiglo and Hass, *l.c.*), and with potassium nitrite and alcoholic caustic potash give *gem*-dinitro-compounds (ter Meer, *ibid.* 1875, 8, 1080).

Chlorination of the nitroparaffins under the influence of phosphorus pentoxide and intense illumination causes replacement of hydrogen atoms other than those on the  $\alpha$ -carbon atom (Hass and Riley, *l.c.*), but bromine gives the same products as under basic conditions.

Other methods for the preparation of aliphatic chloronitro-compounds include the treatment of nitro-alcohols with phosphorus pentachloride and many obvious variations of the synthetic procedures already described (cf. Hass and Riley, *l.c.*).

(h) *Reaction with Diazo-compounds*.—Diazonium salts react with the salts of primary and secondary nitro-compounds in the absence of excess alkali to give hydrazones (IX) and azo-compounds (X) respectively:

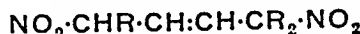


In the presence of excess alkali, a second  $\alpha$ -hydrogen atom in primary derivatives is replaced.

## II. POLYNITRO-COMPOUNDS.

Liquid-phase and low temperature (20–200°) vapour-phase nitrations of paraffins often yield polynitro-compounds in which the nitro-groups may be attached either to the same or different carbon atoms (Ellis, *op. cit.*). Compounds of the latter type have also been prepared by the

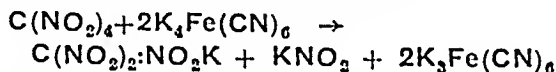
Victor Moyer procedure and by other reactions [I, Reactions (a), (d), (g); III, Preparation (a), Reaction (g)]. In addition, 1:2-dinitro-compounds have been obtained by the electrolysis of the salts of mononitro-compounds (Nenitzescu, *ibid.* 1929, 62 [B], 2669). Apart from 1:2- and 1:4-dinitro-compounds of the constitution



which are exceptional in that they can be converted into unsaturated compounds by loss of nitrous acid [III, Preparation (a)], this type of polynitro-compound is similar in chemical properties to the mononitro-compounds.

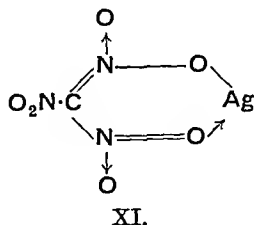
The preparation of *gem*-dinitro-compounds by the oxidation of  $\psi$ -nitroles and by treatment of an  $\alpha$ -halogenonitro-compound with potassium nitrite and alcoholic potassium hydroxide has already been mentioned [I, Reactions (a); (g)]. They can also be obtained (a) by the action of nitric acid on secondary alcohols, ketones, and alkylacetoacetic esters (diethylcarbinol, diethyl ketone, and ethyl methylacetoacetate all yield 1:1-dinitroethane), (b) by the nitric acid oxidation of saturated monocarboxylic acids which contain a tertiary carbon atom (isobutyric and isovaleric acid both yield 2:2-dinitropropano) and (c) by the reduction of  $\alpha$ -halogeno-dinitroparaffins with ammonium sulphide or arsenious acid. Dinitromethane is unstable but the higher members can be distilled without decomposition. The primary dinitro-compounds (*i.e.*, those containing an  $\alpha$ -hydrogen atom) are strong acids and almost certainly exist in the *aci*-form in aqueous solution. Their salts are yellow in colour, yield  $\alpha$ -halogeno derivatives with halogens, and couple with diazonium compounds. The potassium salt of dinitromethane has been condensed with aliphatic aldehydes to give alcohols, and with aldehyde-ammonia to give 1:1-dinitro-2-aminopropano. Reduction of the primary compounds with tin and hydrochloric acid yields carboxylic acids, *e.g.*, 1:1-dinitroethane gives acetic acid. Secondary compounds similarly yield ketones. With aluminium amalgam, one nitrogen atom is readily lost giving an oxime which can be further reduced to an amine.

Nitroform (trinitromethane) is best prepared from tetranitromethane and potassium ferrocyanide; smooth reaction gives the potassium salt of nitroform in quantitative yield:



Potassium hydroxide or potassium oxohydroxide may also be used, but this is a very dangerous procedure owing to the risk of violent explosions. The potassium salt gives free nitroform with dilute sulphuric acid. Higher trinitroparaffins have been obtained from the silver salt of nitroform and alkyl iodides. Nitroform is strongly acidic in aqueous solution, indicating the presence of the *aci*-form. Its mercury and silver salts are remarkable in that they are soluble in most organic solvents; possibly they have the chelated structure (XI) (N. V. Sidgwick, T. W. J. Taylor, and W. Baker, "Organic Chemistry of Nitrogen," Oxford University

Press, 1942, p. 246). The higher trinitro-paraffins, which cannot form salts, are converted into dinitroparaffins by alkalis.



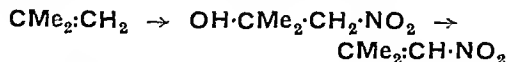
XI.

Tetranitromethane (*cf.* Sidgwick *et al.*, *op. cit.*) has been obtained by nitration of many compounds including acetylene and nitroform, but is best prepared from acetic anhydride and anhydrous nitric acid (Organic Syntheses, 21, 105). It is stable when pure and boils without decomposition, but cannot safely be mixed indiscriminately with other organic compounds; thus with toluene violent explosions have been reported (Stettbacher, J. Ind. Hyg. (Abstr.), 1943, 25, 49 (2)); acid reducing agents give guanidine. Tetranitromethane is used to test for the presence of double bonds since it gives yellow to brown-red colours with most unsaturated and aromatic compounds; nitro- and carboxyl groups often inhibit this reaction. Its use for the nitration of olefinic compounds is referred to below; it will also nitrate the aromatic nucleus in dimethyl-*p*-toluidine and phenols, but in the presence of pyridine *tert*-arylamines give N-nitroso derivatives of the corresponding alkylarylamines, *e.g.*, dimethylaniline gives N-nitrosomonomethylaniline (Schmidt and Fischer, Ber. 1920, 53 [B], 1529, 1537).

### III. $\Delta^{\alpha}$ -NITRO-OLEFINS AND THEIR DERIVATIVES.

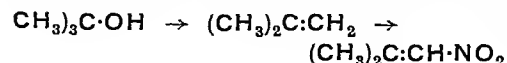
#### Preparation.

(a) *From Unsaturated Hydrocarbons.*—The direct nitration of olefinic compounds takes place much more readily than that of the paraffins. Thus, *isobutene*, *aa*-diphenylethylene, trimethylethylene, ethyl  $\beta\beta$ -dimethylacrylate, and ethyl *p*-nitrocinnamate all give  $\Delta^{\alpha}$ -nitro derivatives on treatment with nitric acid. There is no doubt that the mechanism of the reaction is addition of nitric acid followed by dehydration of the resulting nitro-alcohol, *e.g.*,



The intermediate alcohol and its nitrate can often be isolated from the reaction product and the former is readily dehydrated to the unsaturated nitro-compound.

The production of nitro-olefins by treatment of tertiary alcohols such as *tert*-butyl alcohol and benzyldimethylcarbinol with nitric acid is clearly a similar reaction which depends upon the initial formation of an unsaturated compound:



The treatment of certain styrene derivatives with tetranitromethane in pyridine gives the corresponding  $\beta$ -nitrostyrene (Schmidt *et al.*, *ibid.* 1922, 55 [B], 1751).

$\Delta^{\alpha}$ -Nitro-olefins are often obtained from the products of interaction of nitrous fumes (or nitrogen peroxide) and olefins (Priebis, Annalen, 1884, 225, 327; Lipp, *ibid.* 1924, 449, 15; Michael and Carlson, J. Org. Chem. 1939, 4, 169; 1940, 5, 1). They are apparently produced by the spontaneous decomposition of the primary addition products (XII) and (XIII),

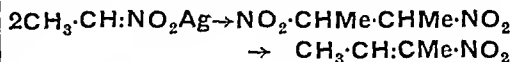


XII.



XIII.

since it is known that many compounds of this type yield nitro-olefins with extreme ease (Gabriel, Ber. 1885, 18, 2438; Wieland and Bloch, Annalen, 1905, 340, 63; Wieland, *ibid.* 1903, 328, 187). It appears probable that the formation of 2-nitro-2-butene by the decomposition of the silver salt of nitroethane (Angeli and Alessandri, Chem. Zentr. 1910, II, 731) proceeds through the intermediate formation of 2:3-dinitro-*n*-butane, since this is also isolated:



In most cases, however, these addition products are more stable, but can usually be converted into nitro-olefins by the action of caustic alkali (Wieland, *l.c.*).

A number of dinitro-olefins have been obtained by treatment of 1:3-dienes with nitrogen peroxide. Thus, 1:4-diphenylbutadiene gives 1:4-dinitro-1:4-diphenyl-2-butene (Wieland and Stenzl, *ibid.* 1908, 360, 299; Ber. 1907, 40, 4828) while 2:3-diphenylbutadiene gives both 1:4-dinitro-2:3-diphenyl-2-butene and 1:2-dinitro-2:3-diphenyl-3-butene (Allen, Eliot, and Bell, Canad. J. Res. 1939, 173, 75). Butadiene itself yields 1:4-dinitro-2-butene (I.C.I. B.P. 532686). Dibenzalacetone gives a 1:2-dinitro-compound. Here again, treatment with caustic alkali may remove nitrous acid; thus, 1:4-dinitro-1:4-diphenyl-2-butene gives 1-nitro-1:4-diphenylbutadiene (Wieland and Stenzl, *l.c.*).

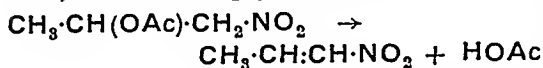
Acetylene derivatives such as phenylacetylene and toluene with nitrogen peroxide yield 1:2-dinitro-olefins, *viz.*,



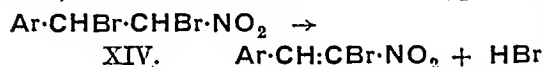
(Wieland, Annalen, 1921, 424, 71; Schmidt, Ber. 1901, 34, 619), and nitril chloride reacts with phenylacetylene to give  $\beta$ -chloro- $\alpha$ -nitrostyrene (Steinkopf and Kühnel, *ibid.* 1942, 75 [B], 1323).

(b) *From Nitro-alcohols.*—Nitro-alcohols derived from aromatic aldehydes and primary aliphatic nitro-compounds are normally dehydrated with extreme ease to give an unsaturated nitro-compound, but those derived from aliphatic aldehydes are usually much more stable and need a powerful dehydrating agent such as thionyl chloride, phosphorus pentoxide, potassium bisulphate, acetic anhydride or zinc

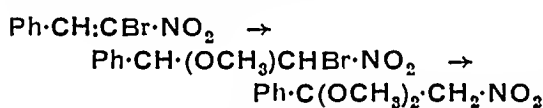
chloride. In the latter case the yields of nitro-olefin are often poor owing to the formation of polymeric by-products. Excellent yields can be obtained very easily, however, by the abstraction of organic acid from the esters of the nitro-alcohols by heating with a trace of a weakly basic substance such as potassium carbonate or sodium acetate (Gen. Aniline and Film Corp., U.S.P. 2257980; Hass, and Riley, *l.c.*; cf. Schmidt and Rutz, *Ber.* 1928, 31 [B], 2142): *e.g.*,



Some inorganic esters of nitro-alcohols have also been converted into  $\Delta^a$ -nitro-olefins by heating alone or with phosphorus pentoxide (Wilkendorf and Trenel, *ibid.* 1924, 57 [B], 306; Wieland and Sakellarios, *ibid.* 1920, 53 [B], 201). In a similar manner, many 1:2-dibromonitro-compounds of type (XIV) give 1-bromo-1-nitro-olefins on treatment with mild alkalis (Thiele and Haackel, *Annalen*, 1902, 325, 1; Worrall and Tatilbaum, *J. Amer. Chem. Soc.* 1942, 64, 1739). Bromonitro-olefins of this type are



useful starting materials for the synthesis of  $\alpha$ -nitroketones, the acetals of which they give on heating with alcoholic potassium hydroxide:

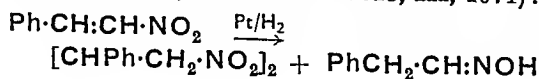


### Physical Properties.

The  $\Delta^a$ -nitro-olefins are almost colourless when pure and their boiling-points are of the same order as the corresponding saturated compounds. Many of the lower members are strongly lachrymatory and polymerise readily. Polymerisation is catalysed by water and alkalis and in some cases occurs with almost explosive violence. Many substituted nitro-olefins (*e.g.*,  $\beta$ -nitrostyrene) also polymerise readily under the influence of a base. The structure of the polymers is unknown. Catalytic hydrogenation of a polymer from 2-nitropropene has given a water soluble polymer containing primary amino groups (Blomquist, Tapp, and Johnson, *ibid.* 1945, 67, 1519).

### Reactions.

(a) *Reduction*.—No general method for the reduction of  $\Delta^a$ -nitro-olefins to the corresponding saturated compounds has yet been reported, although the quantitative conversion of 1-nitro-octene to 1-nitro-octane by hydrogen and a platinum catalyst is described by De Mauny (*Bull. Soc. chim.* 1940, [v], 7, 133). Hydrogenation of  $\beta$ -aryl- $\Delta^a$ -nitro-olefins in the presence of platinum gives dimolecular products, together with small amounts of oximes (Sonn and Schellenberg, *Ber.* 1917, 50, 1513; Kohler and Drake, *J. Amer. Chem. Soc.* 1923, 45, 1281; Banus and Vila, *Chem. Zentr.* 1923, III, 1074):



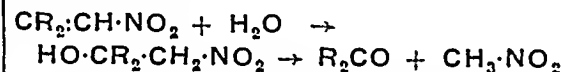
$\Delta^a$ -Nitro-olefins are not easily reduced to the corresponding saturated amines in good yield (*cf.* Hass, *Ind. Eng. Chem.* 1943, 35, 1151). Several successful processes depend upon the initial preparation of the oximo (*see infra*) followed by its reduction, but the yield in the second stage may be poor. Electrolytic reduction of compounds such as  $\beta$ -nitrostyrene and  $\beta$ -2-furylnitroethyleno gives good yields in many cases and is to be preferred to chemical methods (Takamoto, *J. Pharm. Soc. Japan*, 1928, 48, 22; *Chem. Zentr.* 1928, I, 2399; Slotta and Haberland, *Angew. Chem.* 1933, 46, 766; Slotta and Szyzka, *J. pr. Chem.* 1933, [ii], 137, 339). Catalytic reduction in a mixture of acetic and concentrated sulphuric acids has given good yields of amines from  $\beta$ -nitrostyrene (or  $\alpha$ -nitrostilbene) and its derivatives (Kindler *et al.*, *Annalen*, 1934, 511, 209; *Arch. Pharm.* 1935, 273, 478; cf. Schales, *Ber.* 1935, 68 [B], 1579).

$\Delta^a$ -Nitro-olefins are reduced to saturated oximes by zinc dust and dilute acetic acid, aluminium amalgam, and, in some cases, by iron and water (Bouveault and Wahl, *Bull. Soc. chim.* 1903, [iii], 29, 643; Nightingale and James, *J. Amer. Chem. Soc.* 1944, 66, 352; Rosenmund, *Ber.* 1909, 42, 4780; 1910, 43, 3412; Wieland, *Annalen*, 1921, 424, 71; Purdue Res. Foundation, U.S.P. 2233823):

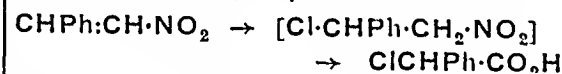


Reduction of nitro-olefins such as  $\beta$ -nitrostyrene and  $\alpha$ -nitrostilbene with hydrogen and palladised charcoal in pyridine also gives oximes in excellent yield (Reichert and Koch, *Arch. Pharm.* 1935, 273, 265; Reichert, G.P. 629313; *idem*, *Arch. Pharm.* 1936, 274, 505).

(b) *Hydration*.— $\Delta^a$ -Nitro-olefins undergo hydrolytic fission at the double bond under the action of dilute sulphuric acid, hydrochloric acid, caustic alkalis, aqueous ammonia, barium hydroxide, and, in some cases, even with water alone. Fission is preceded by hydration at the double bond and if cold dilute sulphuric acid is employed, the intermediate nitro-alcohol can be isolated, *e.g.*,



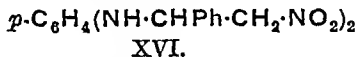
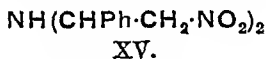
(c) *Addition of Hydrogen Halides*.—The available evidence suggests that these add to nitro-olefins normally, but the expected products have not so far been isolated. Thus action of fuming hydrochloric acid on nitrostyrene gives phenylchloroacetic acid, formed, presumably by hydrolysis of the addition product (Priobs, *Annalen*, 1884, 225, 319):



The addition product of hydrogen chloride and nitrotrimethylethylene has been condensed without isolation with sodium thiophenato to give the expected phenyl nitroamyl sulphide (Michael and Carlson, *J. Org. Chem.* 1939, 4, 169).  $\beta$ -2-Furylnitroethyleno gives  $\epsilon$ -nitro- $\gamma$ -keto-*n*-hexoic acid by fission of the furan nucleus (Thiele and Landors, *Annalen*, 1909, 389, 300).

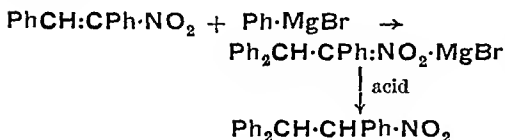
(d) *Addition of Halogens.*—The simple nitro-olefins readily add chlorine or bromine in the cold to give stable dihalogeno derivatives (Haitinger, *ibid.* 1878, 193, 366; Priebis, *l.c.*; Schmidt and Rutz, *l.c.*; Hass and Riley, *l.c.*). Negatively substituted  $\Delta^a$ -nitro-olefins react less readily, and in some cases addition may be prevented entirely.

(e) *Addition of Ammonia and Organic Bases.*—Many  $\Delta^a$ -nitro-olefins react with ammonia, and both aliphatic and aromatic primary and secondary amines, with the formation of  $\alpha$ -aminonitro-compounds (Wieland and Sakellarios, Ber. 1919, 52 [B], 900; Kodak, U.S.P. 2206885; B.P. 539070; U.S.P. 2253082). In most cases, the reaction is facile and proceeds in the cold. When aromatic amines are used, the products are usually fairly stable, but unstable compounds often result with ammonia and aliphatic amines.  $\beta$ -Nitrostyrene (but not all of its nuclear substitution products) reacts with ammonia and *p*-phenylenediamine to give the dinitro-compounds (XV) and (XVI) respectively (Worrall, J. Amer. Chem. Soc. 1927, 49, 1598). Phenyl-

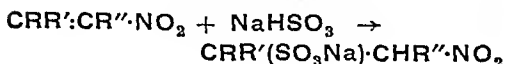
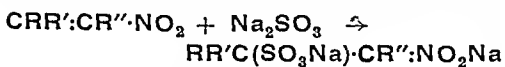


hydrazine, hydroxylamine, and semicarbazide have been similarly condensed with  $\beta$ -nitrostyrene (Posner, Annalen, 1912, 389, 114; Worrall, *l.c.*). Polymerisation of the nitro-olefin may also occur under the influence of the amine and is sometimes the main reaction. Decomposition of the products is favoured by the presence of halogens  $\alpha$ - to the nitro-group, thus, 1-nitro-1-bromo-1-butene and 1-nitro-1-bromopentene are converted into 1-nitro-1-butyne and 1-nitro-1-pentyne, respectively, by heating with methylamine (Loevenich, Koch, and Pucknat, Ber. 1930, 63 [B], 636).

(f) *Addition of Grignard Reagents.*— $\Delta^a$ -Nitro-olefins react with Grignard reagents to form salts of saturated nitro-compounds from which the free nitro-compounds are liberated by treatment with acid, *e.g.*, phenyl magnesium bromide and  $\alpha$ -nitrostilbene yield 1-nitro-1:2:2-triphenylethane (Kohler and Stone, J. Amer. Chem. Soc. 1930, 52, 761; cf. I.C.I., B.P. 571804).

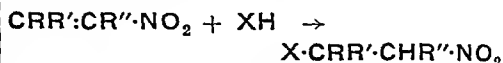


(g) *Addition of Bisulphites and Sulphites.*—Many  $\Delta^a$ -nitro-olefins add sodium sulphite and bisulphite to form the di- and mono-sodium salts of  $\beta$ -nitroalkanesulphonic acids respectively:

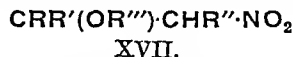


These can be reduced to amines by catalytic means (I.C.I., B.P. 571157).

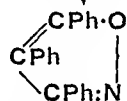
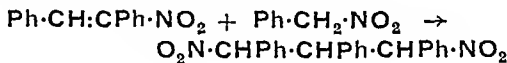
(h) *Addition of Other Reagents.*—In their reactions with a large number of compounds containing reactive hydrogen, the behaviour of  $\Delta^a$ -nitro-olefins is similar to that of  $\alpha\beta$ -unsaturated ketones, nitriles, or esters. Addition takes place across the double bond in the direction shown below:



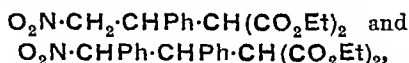
With alcohols in the presence of an alkaline catalyst, ethers of type (XVII) are produced (Commercial Solvents Corp., U.S.P. 2393827).



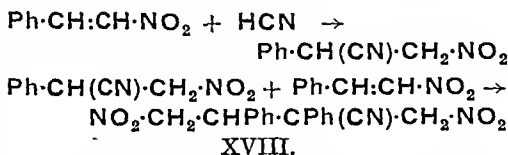
A number of primary and *sec*-nitroparaffins and their derivatives react with  $\Delta^a$ -nitro-olefins to give 1:3-dinitropropane derivatives, *e.g.*, under the influence of a strong base  $\alpha$ -nitrostilbene and phenylnitromethane give 1:3-dinitro-*s*-triphenylpropane which on further treatment with strong alkali gives triphenylisooxazole



Malonic ester adds to  $\beta$ -nitrostyrene and  $\alpha$ -nitrostilbene to give the compounds

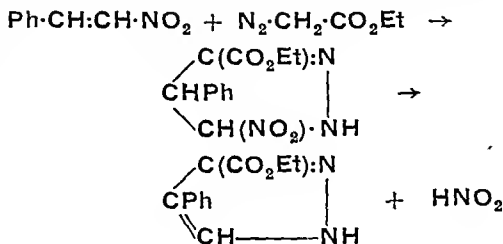


and  $\beta$ -nitrostyrene with excess potassium cyanide followed by acidification gives two stereoisomeric 1:4-dinitro-2-cyano-2:3-diphenylbutanes (XVIII) (Holleman, Rec. trav. chim. 1904, 23, 283); presumably the mechanism of this reaction is:

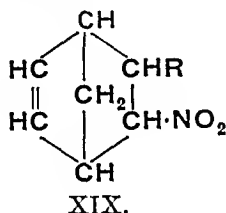


Acetone has been condensed with 1-nitro-2-methylpropene to give 5-nitro-4:4-dimethylpentanone (Hass and Riley, *l.c.*).

Diazoacetic ester combines additively with  $\beta$ -nitrostyrene under the influence of heat to form ethyl 4-phenyl-3-pyrazole-carboxylate (Kohler and Steele, J. Amer. Chem. Soc. 1919, 41, 1104):



(i)  $\Delta$  -Nitro-olefins in the Diels-Alder Synthesis. —Nitroethylene, 1-nitropropylene, and 1-nitropentene add cyclopentadiene smoothly at 100–110° to give cyclic products of type (XIX) in excellent yield (Alder, Rickert, and Windemuth, Ber. 1938, 71 [B], 2451).



Similar adducts are obtained with butadiene and 2:3-dimethylbutadiene, also from  $\beta$ -nitrostyrene and butadiene, isoprene, 2:3-dimethylbutadiene, 2:3-diphenylbutadiene, 1:3-cyclohexadiene, 1:3-diphenylisobenzofuran, 1:3-diphenyl-5:6-dimethylisobenzofuran, and 1:1'-bicyclohexene (Allen *et al.*, J. Amer. Chem. Soc. 1939, 61, 521; J. Org. Chem. 1943, 8, 373).

#### IV. USES OF ALIPHATIC NITRO-COMPOUNDS.

The normal development of the nitroparaffins has been hindered by the war, and it is not easy at present to say what their final applications are likely to be. According to the Commercial Solvents Corporation and their associates of the Purdue Institute, they are solvents for nitrocellulose, organic esters of cellulose, "Vinylite" and other resins, and many oils, fats, and waxes. They are being used commercially as solvents for "Hycar OR," an oil-resistant synthetic rubber; "Buna N" and "Chemigum" are soluble in 1-nitropropane. In this respect, their value is said to lie not only in their high solvent power (which permits considerable dilution by cheaper materials such as alcohol and hydrocarbons) but also in their mild odour, low toxicity, medium rate of evaporation, and comparatively low inflammability. Their use as selective solvents in the refining of petroleum has also been described (Shell Development Co., U.S.P. 2023375; 2019772; see p. 490b).

The nitro-alcohols and their esters are also excellent solvents for cellulose esters. 2-Nitro-2-methyl-1-propanol is an effective heat sensitizer for synthetic and natural rubber latices and for similar dispersions of some of the important substitutes for rubber, and nitroethane, 1-chloro-1-nitropropane, and 2-nitro-2-methyl-1-propanol confer stability on accelerated rubber cements. The potential value of the trinitrate of trimethylol nitromethane as an explosive has already been mentioned (see p. 491b).

The amino-alcohols, formed by reduction of the nitro-alcohols, are of interest both as such, and as their fatty-acid salts, as dispersing, emulsifying, and cleansing agents. This is a field in which the lowest stable homologues, the ethanolamines (made from ethylene oxide or chlorohydrin) have already found considerable application.

Chloropierin, which can now be made from nitromethane instead of wastefully from picric acid, is employed as a fumigant and soil sterilising agent. 1:1-Dichloronitroethane ("Ethide")

is also used for this purpose and is said to be equally as effective as chloropierin but pleasanter to handle. 1-Chloro-1-nitropropane will dissolve many of the new synthetic rubbers, including "Buna N," "Chemigum," and certain neoprenes. Apart from the use as such of the nitroparaffins and their simpler derivatives, it is likely that their future industrial importance will lie in their value in synthesis, *e.g.*, in the preparation of intermediates for the dyestuffs, pharmaceuticals, and allied industries. Thus,  $\beta$ -nitroalkylamines, prepared by the addition of ammonia to  $\Delta^a$ -nitro-olefins, have been employed as intermediates in the preparation of anthraquinone dyes for acetate rayon (Kodak, U.S.P. 2253082). The use of other  $\beta$ -nitroalkylamines derived from aromatic amines and  $\Delta^a$ -nitro-olefins as coupling components in the preparation of azo dyes for cellulose derivatives, silk and wool, and for photographic purposes has also been described (Kodak, U.S.P. 2206885; B.P. 539070); the use of trimethylol nitromethane in photography is covered by Du Pont (B.P. 560253).

Hydroxylamine salts prepared by hydrolysis of 1-nitropropane are now on sale in U.S.A., as are also the nitroparaffins from nitromethane to nitrobutane and a number of their derivatives such as nitro- and amino-alcohols, chloronitroparaffins, and aliphatic amines and acids.

A. L. and H. A. P.

NITROGEN. Sym. N. At. no. 7. At. wt. 14.008. Stable isotopes  $^{14}\text{N}$  and  $^{15}\text{N}$ .

"Der Stickstoff ist das Element der Zukunft" (Brillh, Z. physikal. Chem. 1895, 16, 193).

#### CONTENTS.

- Elementary nitrogen. Nitrides. Active nitrogen (pp. 497d-511b).
- Halides of nitrogen: fluoride; monochloroamine, dichloroamine, nitrogen trichloride; monobromoamine, dibromoamine, nitrogen tribromide; nitrogen iodides (pp. 511b-513c).
- Nitrogen sulphides, trithioazyl compounds, nitrogen selenide (pp. 513c-514d).
- Oxides and oxyacids of nitrogen: nitrous oxide, nitric oxide, dinitrogen trioxide (nitrous anhydride), nitrogen dioxide and dinitrogen tetroxide (nitrogen peroxide), nitrogen pentoxide (nitric anhydride), nitrogen hexoxide or trioxide, nitrous acid (pp. 514d-531a).
- Halides of nitrous acid, nitrosyl fluoride, nitrosyl bromide, nitrosyl tribromide, nitrosyl perchlorate, nitrosyl fluoroborate, nitrosyl hydrogen sulphate (nitrososulphuric acid, or chamber crystals), nitrosyl disulphate (dinitrososulphuric anhydride) (pp. 531a-532d).
- Hyponitrous acid, nitramide, hyponitric acid (nitrohydroxylamic acid), hydronitrous acid (pp. 532d-531c).
- Nitric acid, halides of nitric acid, nitryl fluoride, pernitryl fluoride (fluorine nitrate), nitryl chloride, pernitrous acid (pp. 534e-541e).
- Manufacture of nitric acid by the retort process (pp. 541e-543d).

#### NITROGEN.

##### HISTORY.

J. B. van Helmont (d. 1644) in his posthumous "Ortus medicinae" (1648) describes the extinction of a candle in a confined volume of air over water and the smaller volume of the remaining "gas" (J. R. Partington, Annals of Science, 1936, 1, 359). A similar experiment

was made by J. Mayow ("Tractatus quinque medico-physici," Sheldonian Theatre, Oxford, 1674), who also noticed the contraction of a confined volume of air caused by the respiration of a mouse. C. W. Scheele in 1770-73 first prepared pure atmospheric nitrogen (*foul air*) by absorbing the oxygen (*fire air*) from air, and recognised that it is mixed in the atmosphere with oxygen, which he was probably the first to prepare in a pure state. Daniel Rutherford, Professor of Botany in the University of Edinburgh, found in 1772 that when a small animal is allowed to breathe in a confined volume of air and the carbon dioxide (*mephitic air*) produced is removed by absorption in alkali, another mephitic gas remains which is incapable of supporting respiration. Nitrogen was also obtained by Priestley in 1772 and called by him *phlogisticated air*, a name which was for long in use. Lavoisier established the individuality of the gas and its existence in the atmosphere; from its incapacity to support life he called it *azote* (a name still used in France and symbolised Az, and translated as *Stickstoff* in the German name); the name *nitrogen* was given to it by Chaptal in 1790 to denote that it is an essential constituent of nitre (J. R. Partington, "A Short History of Chemistry," Macmillan, 1939).

#### OCCURRENCE.

Nitrogen is widely diffused but forms less than 1% of the combined composition of the air, sea, and earth's crust. *Free nitrogen* occurs in the atmosphere, of which it constitutes four-fifths, or more accurately 78.06%, by volume (Leduc, Compt. rend. 1896, 123, 805). Volcanic gases may contain considerable quantities of nitrogen, which is also present in mine gases, the gases from springs, and gases occluded in minerals and rocks; it is present in the free state in the air bladders of fish (in which it was discovered by Fourcroy), the bone-cavities of many birds, and cavities in plants. It occurs in many meteorites, in nebulae, and in the atmosphere of the sun. *Combined nitrogen* occurs in the atmosphere as ammonia and nitrous and nitric acids and their salts, and hence these compounds occur in rain-water (R. Angus Smith, "Air and Rain," Longmans, 1872). Oxides of nitrogen are present in the atmosphere in quantities which vary largely from time to time; the amounts are usually rather greater at high altitudes (over 4,000 ft.) than at low altitudes and in summer than in winter, and hence the oxides are probably formed by the action of ultra-violet light (Hayhurst and Pring, J.C.S., 1910, 97, 868; Rao and Dhar, Z. anorg. Chem. 1931, 199, 422). Vorländer and Gohdes (Ber. 1931, 64 [B], 1776) found oxides of nitrogen equivalent to  $22 \times 10^{-6}$  g. of  $N_2O_3$  per cm.m. of moist November air at Halle, and 10-100 times this amount after exposure to ultra-violet light.

Combined nitrogen is an essential component of proteins and other constituents of animal and vegetable organisms, and is found in many minerals, but chiefly in saltpetre or potassium nitrate and Chile saltpetre or sodium nitrate. (On the nitrogen cycle, see NITROGEN, ATMOSPHERIC, UTILISATION OF, this Vol., p. 544a).

#### PREPARATION OF NITROGEN.

Except in small-scale laboratory preparations, nitrogen is extracted from atmospheric air. This may be done either by chemical methods in which the oxygen is removed (a) by some chemical change in which it is absorbed (in which case the argon and other inert gases remain in the nitrogen), or (b) by physical methods, especially the fractional distillation of liquid air (in which case the argon may be largely removed on account of its higher boiling-point). In large-scale working the physical method is almost exclusively used.

The volume percentage composition of dry London air (Paneth, Nature, 1937, 139, 181) is:

N <sub>2</sub>	. . . 78.08	Kr	. . . . . $1.0 \times 10^{-4}$
O <sub>2</sub>	. . . 20.95	Xe	. . . . . $1.0 \times 10^{-5}$
A	. . . 0.93	O <sub>3</sub>	. . . . . $< 1 \times 10^{-6}$
CO <sub>2</sub>	. . . 0.03	Rn (average near	
Ne	. . . $1.8 \times 10^{-3}$	ground)	. . . $6 \times 10^{-18}$
He	. . . $5.0 \times 10^{-4}$	H <sub>2</sub> doubtful but	$< 10^{-4}$

The constancy of the percentages of carbon dioxide and oxygen in uncontaminated atmospheric air was established by Benedict in 1912. T. M. Carpenter has described (J. Amer. Chem. Soc. 1937, 59, 358) several hundred analyses of air made in the period 1930-36 in New Hampshire, Baltimore, and Boston. The grand average of all three series gave 0.031% for carbon dioxide and 20.939% for oxygen. There was no evidence that variations in season or the proximity of large consumers of fuel caused any measurable differences in the carbon dioxide and oxygen contents.

#### (a) Nitrogen from the Atmosphere by Chemical Methods.

There are several old patents specifying the removal of oxygen from air by passing it over heated metals such as iron (Spencer, B.P. 3752, 1869) or copper (Welton, B.P. 2559, 1879; Frank and Fincke, B.P. 10718, 1912; Cyanid-Ges., G.P. 218671, 1908) or molten lead (Nitrogen Co., New York, B.P. 17666, 1911). The use of sulphur (Blagburn, B.P. 25535, 1908) or phosphorus (Haddan, B.P. 24293, 1895) is specified. A satisfactory method is to pass a mixture of air and ammonia gas over heated iron or partly oxidised copper turnings, when the hydrogen of the ammonia burns out the atmospheric oxygen (Carius, Annalen, 1855, 94, 136; Lupton, Chem. News, 1876, 33, 90; Hntton and Petavel, J.S.C.I., 1904, 23, 87; Marston, B.P. 19074, 1900; Farbenw. vorm. Meister Lucius und Brüning, B.P. 3662, 1913; 28737, 1913; 9974, 1914). The atmospheric oxygen may also be removed by hydrogen (Hulett, J. Amer. Chem. Soc. 1905, 27, 1415) or other combustible gas (Bucher, J. Ind. Eng. Chem. 1917, 9, 233), the mixture being passed over heated copper (which may afterwards be reduced by hydrogen or coke-oven gas) or a catalyst such as silicon carbide, and the combustion products may be liquefied, leaving nitrogen (Metzger, assr. to Air Reduction Co., U.S.P. 1588258, 1926).

The atmospheric oxygen may also be removed by a cold absorption method, e.g., by alkaline pyrogallol solution (Liebig, Annalen, 1851, 77, 107) or moist barium sulphide (Alder, B.P.



1004, 1880) or iron filings moistened with ferrous sulphate solution (Wise, B.P. 4359, 1877) or manganous or ferrous hydroxides (Flight, Chem. News, 1882, 45, 105). A very convenient process, which may be made continuous, is to pass air over clean copper turnings kept wetted with aqueous ammonia (Berthelot, Bull. Soc. chim. 1870, [ii], 14, 314; 1889, [iii], 2, 643). An apparatus (see Fig. 1) comprises a reservoir A

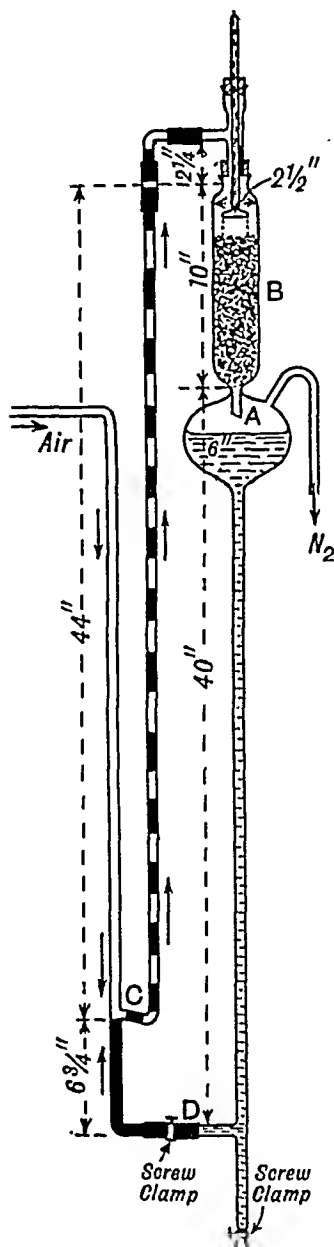


FIG 1.

containing a mixture of equal volumes of a saturated solution of commercial ammonium carbonate and ammonia of  $\rho$  0.93. The liquid flows from A at a rate controlled by the screw-clamp D, and encounters a current of air at the branch C, which should slope as shown. The fall-tube from A must be long enough to give a pressure at C such that the volume of solution carried up is at least equal to that of the accompanying air. The air-liquid mixture is

discharged over the glass ball in the top of B and descends through the copper clippings in B. The air, now freed from oxygen, is freed from ammonia with dilute sulphuric acid (Van Brunt, J. Amer. Chem. Soc. 1914, 36, 1448; J.S.C.I. 1914, 33, 788). A modified form of apparatus uses a solution of ammonia saturated with ammonium chloride (Badger, J. Ind. Eng. Chem. 1919, 11, 1052; Analyst, 1920, 45, 32).

The oxygen may also be absorbed in a solution of ammonium sulphite with a cobaltamine catalyst (Vorländer and Lainau, J. pr. Chem. 1929, [ii], 123, 351).

In most of these cases, after removal of carbon dioxide and water vapour, the gas obtained is at best 99% pure, as inert gases are still present.

The use of heated carbon for removal of oxygen, which amounts to the separation of nitrogen from oxides of carbon in the gas from furnaces or gas producers, has often been proposed (Frank and Caro, G.P. 204882, 1907; B.P. 16963, 1908; Riedel, B.P. 20631, 1909; Braum, B.P. 22531, 1911; Harger, B.P. 16855, 1912; McCourt and Ellis, B.P. 25629, 1912; Dreaper, B.P. 12927, 1913; Brownlee and Uhlinger, B.P. 5097, 1915; Kitzinger, Chem. Trade J. 1918, 62, 88). It is from a modification of this process that nitrogen is largely prepared for ammonia synthesis. The oxygen may also be absorbed by passing air over heated calcium plumbate, alkali manganate, etc. (Kaszner, G.P. 233883 and 234849, 1910).

#### (b) Nitrogen from the Atmosphere by Physical Methods.

Since atmospheric nitrogen and oxygen are mixed in the uncombined state it is, theoretically, possible to separate them by physical processes with a relatively small expenditure of energy (J. R. Partington, "Chemical Thermodynamics," Constable, 1940, p. 50). Many such processes have been proposed, depending, for example, on: (i) the greater rate of passage of oxygen as compared with nitrogen through unvulcanised rubber (Graham, Phil. Trans. 1866, 156, 399; "Chemical and Physical Researches," Edinburgh, 1876, p. 235); (ii) the greater rate of diffusion ("atmosolysis") of nitrogen through porous bodies than of oxygen (*idem, ibid.*, 1863, 153, 385; *op. cit.*, p. 224); (iii) the centrifugal separation of the gases, depending on their different densities (Mazza, 1901, quoted by E. Molinari, "Treatise on Inorganic Chemistry," Churchill, 1920, p. 198; B.P. 423003, 1933; Rabu, L'Industrie Chim. 1935, 22, 896); (iv) the greater solubility of oxygen in water as compared with nitrogen (Mallet, B.P. 2137, 1869; Hélonise, Ber. 1882, 15, 1221); (v) the fractional distillation of liquid air, the nitrogen, which has a lower boiling-point ( $-195.7^\circ$ ) tending to pass off before the oxygen, of boiling-point  $-182.9^\circ$  (*cf. Erdmann, ibid.* 1906, 39, 1207; Stock and Nielsen, *ibid.* 3393; Baly, Phil. Mag. 1900, [v], 49, 517; Inglis, J.C.S. 1906, 89, 886; Phil. Mag. 1906, [vi], 11, 640; Dodge and Dunbar, J. Amer. Chem. Soc. 1927, 49, 591). Of these methods, only the last is used, and it now furnishes practically all the oxygen and a large proportion of the nitrogen used in industry.



The separation of liquid air was first patented by Parkinson (B.P. 4411, 1892); in 1895 William Hampson took out a patent (B.P. 10165, May 23, 1895) a few weeks before Linde's (G.P. 88824, June 5, 1895). Hampson's provisional specification is somewhat ambiguous, and full details of Linde's apparatus were made known before the completion of Hampson's patent. The bases of Linde's process are clearly given in his patent specification (reproduced in *Z. physikal. Chem.* 1896, 20, 638) as: (i) cooling the air to be condensed by causing it to flow in the contrary direction [through a heat interchanger] to the evaporating products; (ii) causing the gaseous air to transmit its latent heat to the evaporating liquid; and (iii) causing the vapours produced in the distilling apparatus to flow upwards through the liquid flowing downwards in a stratified manner.

The fall in temperature necessary for the liquefaction of a gas, which must in any case cool the gas below its critical temperature, may be achieved by two entirely different methods, which must be carefully distinguished.

1. The first of these takes energy from the gas as *external work*, the gas being allowed to expand against a pressure; if the expansion occurs in such a way that heat is prevented from entering the gas from outside, as when the expansion occurs very rapidly, it is called an *adiabatic expansion*, and since in this case the energy of the gas is drawn upon to produce the external work, the gas is cooled. The fall in temperature in adiabatic expansion is independent of the mass of gas used and depends only on the pressures before and after expansion; if these are  $p_1$  and  $p_2$ , respectively, and if  $T_1$  and  $T_2$  are the corresponding *absolute* temperatures, then for an ideal gas:

$$\{(\gamma-1)/\gamma\} \log (p_1/p_2) = \log (T_1/T_2) \quad (1)$$

where  $\gamma = C_p/C_v$ , the ratio of specific heats; a modified equation may be used with an imperfect gas such as oxygen or nitrogen (J. R. Partington, "Chemical Thermodynamics," Constable, 1940, pp. 5, 47, 68, 218). For practical purposes, however, equation (1) may be used for oxygen, nitrogen, or air, with  $\gamma=1.40$ .

2. The second method, discovered and investigated experimentally by Joule and William Thomson (afterwards Lord Kelvin) in 1852-62 (*Phil. Mag.* 1852, [vi], 4, 487; *Phil. Trans.* 1853, 143, 357; 1854, 144, 321; 1862, 152, 579), cools the gas by *internal work*, which is done by separating the molecules, during expansion, under the influence of attractive forces between them. This effect occurs only with a non-ideal gas, and is superposed on the effect of external work if the expansion is carried out adiabatically. This so-called *Joule-Thomson effect* (which vanishes for an ideal gas, between the molecules of which there are no forces acting) will cool the gas if the expansion occurs so that heat cannot enter it from outside. This is achieved by allowing gas compressed in one vessel to escape through a nozzle or throttle into another vessel (or into the atmosphere) where it is at lower pressure. The work  $p_1 v_1$  spent in forcing a volume  $v_1$  of the gas through

the nozzle at a pressure  $p_1$  is practically recovered in the expulsion of the volume  $v_2$  against the lower pressure  $p_2$ , since if the gas obeys Boyle's law approximately,  $p_1 v_1 = p_2 v_2$ , so that practically no *external work* is done by the gas (J. R. Partington, *op. cit.*, p. 58). The fall in temperature  $\Delta T$  for the Joule-Thomson expansion of air initially at the absolute temperature  $T$  with a pressure drop through the nozzle of  $\Delta p$  atm. is given by:

$$\Delta T = 0.276(273/T)^2 \Delta p \quad \dots (2)$$

Hampson and Linde made use of the Joule-Thomson effect in conjunction with a *heat interchanger*. Equation (2) shows that if air at 0°C. expands through a nozzle from 100 atm. to 1 atm. pressure, the fall in temperature is about 25°C. If this air at -25°C. sweeps over the outside of a copper pipe carrying the compressed air to the nozzle, this air is cooled below 0° before expansion, and hence after expansion it is cooled below -25°C. The cooling effect evidently *accumulates*, and the air issuing from the nozzle finally becomes so cold that it liquefies. Linde realised that, since the absolute temperature  $T$  of the expanding air occurs in (2) in the reciprocal of a square, the cooling effect increases very rapidly as the temperature falls (see H. Alt, "Die Kalte," Teubner, Leipzig, 1910, p. 24, for a graphical treatment of equation (2)). The theoretical cooling effect is never attained in practice, on account of the rapid exchange of heat between the cold gas and the warmer surroundings.

The separation of air into its components by liquefaction and fractional distillation was patented by Linde in 1902 (B.P. 14111, 1902; see Kausch, *Z. kompr. u. verfl. Gase*, 1902, 5, 171, 187; 6, 33).

The following table, compiled by Linde, shows that the mere quiescent evaporation of liquid air cannot give a gas ("vapour") sufficiently rich in nitrogen and a liquid residue sufficiently rich in oxygen to make this process of any practical interest. Thus, to obtain a residue containing 50% of oxygen at least 70% of the liquid would have to be evaporated, and an increasing fraction of the oxygen is lost in the vapour as the evaporation proceeds.

% of liquid not evaporated.	% of oxygen in liquid.	% of oxygen in vapour.	% of original oxygen still in liquid.
100.0	23.1	7.5	100.0
50.0	37.5	15.0	80.0
30.0	50.0	23.0	65.0
20.0	60.0	34.0	52.0
15.0	67.5	42.0	43.0
10.0	77.0	52.0	33.0
5.0	88.0	70.0	19.0

The pioneer experiments of Baly (*Phil. Mag.* 1900, [v], 49, 517; Inglis, *ibid.* 1906, [vi], 11, 640) on the compositions of liquid and vapour in equilibrium for nitrogen-oxygen mixtures gave results of great service in the control of technical plant. They are now replaced by the more recent data of Dodge and Dunbar (*J. Amer. Chem. Soc.* 1927, 49, 591), whose curves for

various pressures ( $P$ , in atm.) are reproduced in Fig. 2 (see also M. Ruhemann, "The Separation of Gases," Oxford, 1940). In this the ordinates are absolute temperatures and the abscissæ mol.-% of oxygen. The upper curve of each lens-shaped pair refers to vapour and the lower to liquid, and the pressure in atmospheres at which evaporation is carried out is given for each pair of curves. One square represents  $2^{\circ}\text{C}$ ., and each lens has a separate temperature scale defined by the temperatures shown at its ends; e.g., at 1 atm. pressure the scale extends from  $77\cdot33^{\circ}\text{K}$ . at the lower end to  $90\cdot16^{\circ}\text{K}$ . at the upper end.

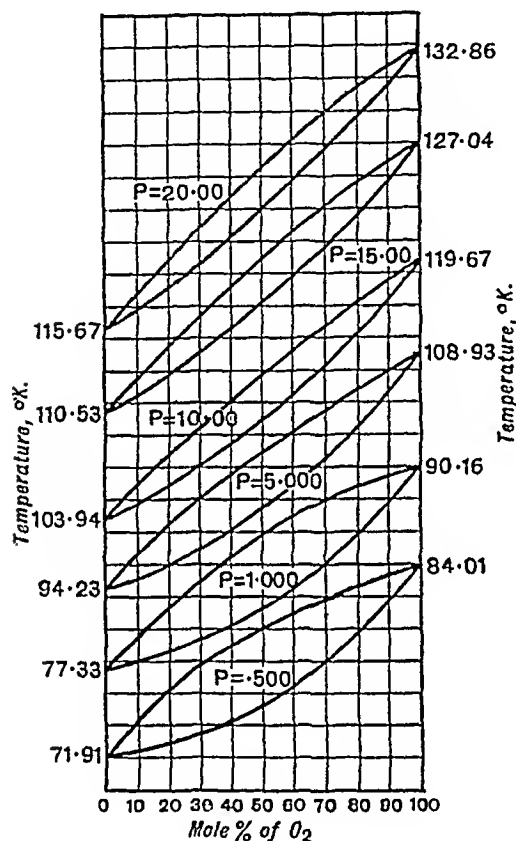


FIG. 2.

The vapour, it is seen, is always richer in nitrogen than the liquid; if a composition point is taken on either curve, the composition of the other phase in equilibrium is found by drawing a horizontal through the chosen point until the other curve is cut. The process used in air separation depends on exactly the same principles as an ordinary fractional distillation (see DISTILLATION, Vol. IV, 34).

Since the apparatus used for the separation of oxygen in Linde's process is simpler than that required for the production of fairly pure nitrogen, it will be described first.

A sectional elevation of a single-column Linde separator is shown in Fig. 3. The rectifying column A, provided with plates, is housed in a circular casing of wood, whilst the vaporising or distilling chamber B is contained in a hexagonal wooden casing, all clearance spaces being packed with heat insulation, e.g., sheep's wool.

The counter-current heat interchanger  $\sigma$  is a wide copper spiral pipe containing three narrow copper pipes  $d$ , one enclosed in a somewhat wider pipe  $e$ . An extension  $c_1$  of the wide pipe delivers to a funnel-end  $F$  at the top of the rectifying column, and  $c_1$  is a funnel-end of  $\sigma$  at the top of the vaporising chamber  $B$ .

The coil  $d_1$  in  $B$  connects at one end with the narrow pipes  $d$  in the interchanger and at the other end with the valve  $\sigma$  which is operated outside the apparatus by  $H$  and delivers to a pipe  $d_2$  connected with a rose-end near the top of  $A$ .

The apparatus is first charged with liquid air as follows: Air at about 2,000 lb. per sq. in. pressure enters through  $D$  into the three pipes  $d$  of the interchanger, passes down these, and

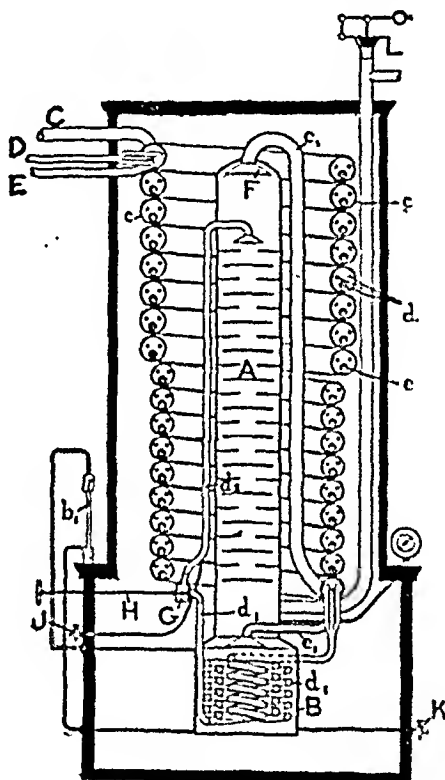


FIG. 3.

through  $d_1$  to the valve  $\sigma$ , through which it expands, passing through  $d_2$  to the top of the column. It then passes through  $c_1$  and  $c_1$  to the interchanger, in a reverse flow to the incoming air, and leaves through  $c$  and  $r$ . Owing to the Joule-Thomson cooling, liquid air forms and drops down into the vaporiser  $B$ . The level of this liquid is indicated by an external gauge  $b_1$ .

The separation process now begins. The air passing through the coil in  $B$  transmits some of its latent heat to the liquid in  $B$ , which is thereby evaporated whilst the compressed air in the coil is itself liquefied in proportion to the amount of heat taken from it. The vapour from the liquid boiling in  $B$  passes up the column and bubbles through the liquid descending past the plates in  $A$ . A temperature gradient is established in  $A$ . The nitrogen, with a lower boiling-point, boils off towards the top of the column, creating the maximum cold there, and the

descending liquid is enriched in oxygen. The ascending gas is scrubbed by the liquid, and at each stage some of the rising oxygen is condensed and some of the nitrogen in the descending liquid is evaporated, so that this liquid, which is gradually rising in temperature, is practically pure oxygen when it reaches *b*.

The gas passing out of the top of the column through *f* is mainly nitrogen at a temperature about  $14^{\circ}$  lower than that of the oxygen at the bottom of the column. The oxygen gas from *b* passes out of *e*, to *e* of the interchanger. The cold gases escape at pressure of about 4–5 lb. per sq. in. *L* is an emergency release valve on the low-pressure system and *J* and *K* are test-cocks communicating with the liquid air and liquid oxygen supplies, respectively.

Linde used a separate fore-cooler, operating with carbon dioxide or ammonia, before the separating column, so that the entering air is

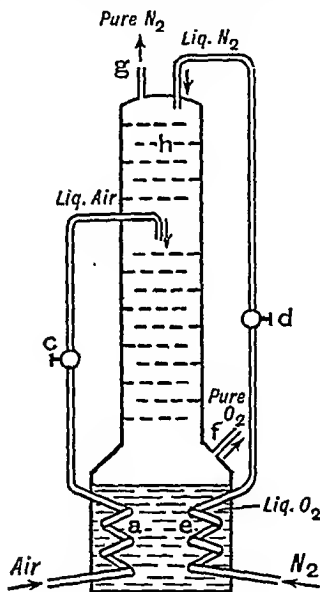


FIG. 4.

cooled well below  $0^{\circ}\text{C.}$  and so dried, and the carbon dioxide of the air is also removed by slaked-lime purifiers before compression. Moisture and carbon dioxide lead to stoppages in the apparatus, as they are solidified at the low temperatures.

By discharging the liquid to the top of the column and allowing it to evaporate under the lower pressure, it is reduced in temperature, and the correct temperature gradient is established in the column. Descending liquid comes in contact at each stage with gas containing more oxygen than corresponds with equilibrium, hence some oxygen is condensed and some nitrogen evaporated.

In order to obtain pure nitrogen Linde withdrew part of the nitrogen gas from the top of the column under atmospheric pressure at *g* (Fig. 4), liquefied it under pressure in the coil *e* in liquid oxygen at the base of the column, and admitted it through the valve *d* to the top of the column. The liquid air condensed under pressure in the coil *a* was admitted through the

valve *e* to that stage in the column where the liquid was of the appropriate composition. In descending the column the liquid lost nitrogen as gas and this was finally scrubbed with the nearly pure liquid nitrogen at the top of the column, with the result that nearly pure nitrogen gas escaped there. As explained, nearly pure liquid oxygen collects in the base, nearly pure oxygen gas being taken off at *f*. This single-column apparatus was replaced by the double column, but as this incorporates a feature present in the simple form of Claude's rectifier, this will first be considered.

In Claude's process (Compt. rend. 1905, 141, 823; G. Claude, "Liquid Air, Oxygen, Nitrogen," Churchill, 1913) two new features are introduced:

- (i) The air is separated by condensation into two liquids, one richer in oxygen and the other in nitrogen, these being discharged into appropriate places in the rectifying column;
- (ii) the air is cooled by expanding it from 20–35 atm. pressure to 4–5 atm. pressure in an engine cylinder, the external work done by the engine taking energy from the air and so causing its temperature to fall.

The initial pressure used is thus much less than that used in Linde's apparatus with nozzle expansion, and the fore-cooler is not necessary, since the temperature exchangers for the cold nitrogen and oxygen gases leaving the separator are used alternately as refrigerators and dry the incoming air.

The effective temperature obtainable by expansion in an engine is about  $-140^{\circ}\text{C.}$  since, owing to the rapid increase in the deviation from Boyle's law, expansion at lower temperatures occurs with very little expenditure of work, and work may even be absorbed in overcoming mechanical friction. Since the critical point of air is at about  $-140^{\circ}\text{C.}$  and 39 atm. pressure, it is possible, by allowing the expanded air cooled to about  $-140^{\circ}$  to cool air at 40 atm. pressure which has previously been cooled in an interchanger, to liquefy this compressed air, and by releasing the pressure to atmospheric the liquid cools itself to  $-190^{\circ}$  by partial evaporation. By adjusting the height of liquid in the liquefier-temperature interchanger, which height controls the rate of liquefaction, the air enters the expansion engine at about  $-10^{\circ}$  (B.P. 27658, 1902). Lubrication of pistons at such temperatures is difficult, but it was found that specially treated leathers can be used without lubrication.

In Claude's apparatus (Fig. 5) air at about 20–35 atm., cooled by an interchanger, enters *A* already partly liquefied and passes through two sets of vertical pipes. The first drain into *A* and the second form a ring round the first and drain into *C*. Both sets are immersed in the bath *S* which, when the machine is operating, contains nearly pure liquid oxygen. The compressed air rises in the central group of tubes in *S*, and a liquid rich in oxygen condenses, which drains into *A*. The gaseous residue passes through the outer ring of tubes, is liquefied in

them, and the liquid rich in nitrogen falls into an annular tube and pot c. This liquid is taken to the top of the column, that in A to a lower compartment L containing scrubbed liquid of the same composition. Gas rich in nitrogen passes from the top of the column and its cold is used in interchangers. The liquid condensed in the inner tubes in s is scrubbed by the air passing on.

The heat of condensation of the compressed air evaporates the liquid oxygen in s, part of the vapour going up the rectifying column D in which it is mostly condensed, the heat of condensation displacing nitrogen from the liquid,

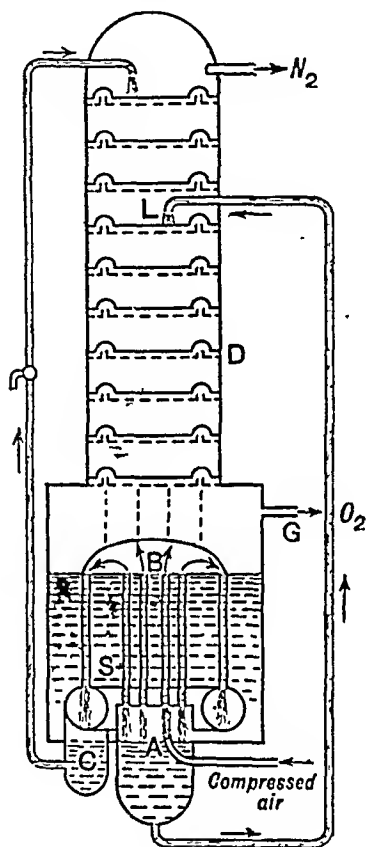


FIG. 5.

which flows into s. The oxygen gas from s goes off by g to the heat interchanger, where its cold is utilised, after which it is pumped under pressure into steel cylinders for sale.

Part of the compressed air is not put through the expansion engine but, after pre-cooling in an interchanger by the very cold oxygen and nitrogen gases from the separator, is liquefied by expansion through a nozzle, and the liquid is fed to the bottom of the vaporiser with the cold air from the expansion engine. Thus the requisite quantity of liquid is maintained, and at the same time, by adjusting the flow through the nozzle, the supply of compressed air to the engine can be regulated at will. This is important, since if the temperature of the air after passing through the engine approaches that of liquid air, the expansibility is so reduced that the cooling produced by the engine is of little value.

Linde's double column apparatus (G.P. 203814, 1906; H. C. Greenwood, "Industrial Gases," 1920, p. 86) makes use of two rectifying columns (Fig. 6, in which the plates in the columns are omitted for clearness), separated by an apparatus for fractional condensation in tubes in an oxygen-bath, like that used by Claude. The lower column A operates under 4 atm. pressure and in it a liquid containing about 35-40% of oxygen separates. The upper column B works under a lower pressure, and hence in it the temperature is lower. The pre-cooled air under pressure is completely liquefied in the coil a and the liquid is discharged through a regulating valve b to

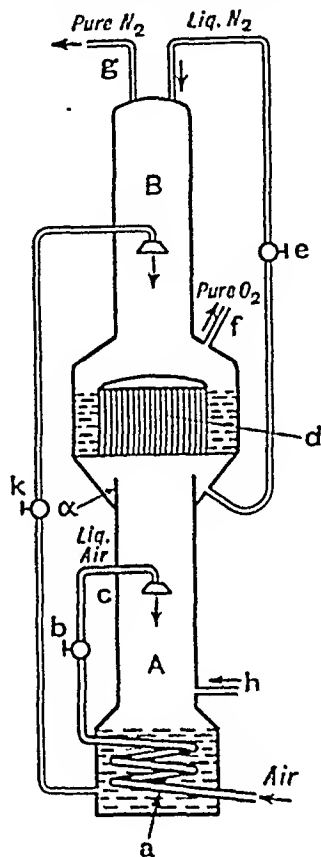


FIG. 6.

the middle of the lower column at c, from where it descends over the plates to the base of the column, where the liquid (35-40% oxygen) is evaporated by the latent heat of the air liquefying in the coil a. Alternatively, gaseous air may be admitted at h.

The vapour rises through the column A, giving up its oxygen to the descending liquid and becoming enriched in nitrogen, so that at the top of the column A almost pure nitrogen condenses (under pressure) in the nest of annular tubes in the liquid oxygen bath d. About half of this liquid rich in nitrogen drains into A and scrubs oxygen from the rising vapour; the other half collects in the annulus a, from which it passes through the valve o to the top of the upper column B.

An approximately equal volume of liquid with 35-40% oxygen from the base of A is admitted through the valve k to the appropriate plate at

about the middle of the column B. Finally, nearly pure liquid oxygen collects in d, and is evaporated by the latent heat of the nitrogen condensing in the tubes. About one-fifth of this vapour is taken off as nearly pure oxygen gas at f and the rest rises through the column B. The vapour from B escapes at g as practically pure nitrogen, the cold of the gases from f and g being used in exchangers. In the condenser d there is almost complete liquefaction; the small amount of uncondensed helium and neon can be separately treated by taking off the gas (about 80% nitrogen) at the top of the condenser.

The apparatus is actually worked either for pure oxygen or pure nitrogen, the difference depending mainly on the position in the column B where liquid is admitted, this being rather lower for nitrogen than for oxygen, and the manipulation of the off-take valves for the gases, the purity of the gas being increased when the amount taken off is reduced as compared with the other gas. Thus, either 99.8% oxygen, or nitrogen with less than 0.1% of oxygen, can be obtained. It is difficult to obtain both gases pure simultaneously owing to small irregularities in the functioning of the column, but by careful regulation 99% oxygen, and nitrogen with 1%

of oxygen, can be obtained simultaneously. If the oxygen is to be argon-free, the nitrogen will contain 1.2% of argon, and if the nitrogen is to be argon-free the oxygen will contain 4.3% of argon. If argon is to be made, it is collected in the oxygen, and the mixture separated in another apparatus (*v. ARGON*, Vol. I, 461d). Patents for the simultaneous production of pure oxygen and nitrogen have been granted but are, apparently, not much used.

The Pictet process (F.P. 295002, 1899; Maxted, J.S.C.I. 1917, 36, 777; H. C. Greenwood, *op. cit.*, p. 90) is said to operate economically, and modifications of the Linde process incorporating an expansion engine have been introduced by Fränkl and by Heylandt, whose process produces liquid oxygen.

There is apparently little to choose in the working efficiencies of the modern Linde and Claude plants. The low working pressure and rapidity in starting of the Claude plants have been quoted in its favour, and one estimate (H. C. Greenwood, *op. cit.*, p. 77) quotes an output of 0.75 l. of liquid oxygen per kw.-hr. at the switchboard, as compared with 0.65 l. for the Linde plant. A more recent set of figures (Ullmann, "Enzyklopädie der technischen Chemie," 1932, Vol. IX, p. 96) is given below.

Cu.m. 99.5% O <sub>2</sub> per hour . . . . .	10	50			100				500			1,000
Type . . . . .	A	A	B	D	E	F	C	H	E	F	C	F
Energy at com- pressor shaft h.p.- hr. :												
(a) for cooling.	31	136	93	96	157	100	110	—	—	400	500	750
(b) in working state . . . . .	23	104	72	70	122	108	100	180	570	450	440	860
(c) do. per cu. m. of O <sub>2</sub> . . . . .	2.3	2.1	1.46	1.4	1.2	1.1	1.0	1.8	1.14	0.9	0.9	0.86
Cooling water, cu.m. per hr. . . . .	1.5	5.5	4	4.5	7.5	6.5	5.5	9.1	36.5	30	22	55

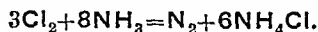
The types A, B, D, E, and F operate by the Joule-Thomson effect, A and B without pre-cooling and with initial pressures of 200 atm. for filling with liquid air and 35–80 atm. in operation; A is a single-column, and B a double-column apparatus; D operates with ammonia pre-cooling and a working pressure of 35–40 atm.; E is a large plant in which a pressure as low as 20 atm. can be used. F denotes plants working by compressing 15–30% of the air to 200 atm. and the rest to about 5 atm., with ammonia pre-cooling, and these are most suitable for large-scale operation. C denotes Claude plants (having about the same efficiency as F), and H a Heylandt plant producing liquid oxygen with expansion (1.31 kg. of liquid oxygen = 1 cu.m. of gas). The table also applies approximately to nitrogen production if the gas volumes are multiplied by four. For 1 cu.m. of nitrogen in F apparatus giving 500–2,000 cu.m. per hour, the energy requirement is 0.2–0.28 h.p.-hr. on the compressor shaft. For nitrogen, practically only two-column rectifiers are used except for small installations of less than 60 cu.m. per hour capacity, and the two-column apparatus is of the two main types, (i) D or E

with 60 atm. maximum pressure and 20–30 atm. working pressure, and (ii) F with high- and low-pressure air; type (i) for 500–2,000 cu.m. per hour of nitrogen and 0.28 h.p.-hr. per cu.m., and type (ii) for larger installations and 0.2–0.28 h.p.-hr. per cu.m. It is important in connection with nitrogen fixation industries to bear in mind that in making pure nitrogen an enriched air with only 50–70% of oxygen may very economically be obtained as a by-product, and this can find very useful application in modern processes.

### (c) Nitrogen from Chemical Compounds.

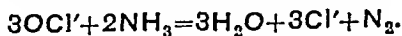
Nitrogen free from inert gases and (when prepared by a suitable process) in a high state of purity, may be obtained from its compounds. Many processes for this preparation involve the removal of hydrogen from ammonia by an oxidation process:

1. By passing chlorine into excess (otherwise explosive nitrogen trichloride may be formed) of concentrated ammonia (Fourcroy, 1789):



Ammonia is removed by passing the gas (which always contains a little oxygen: Anderson, *Chem. News*, 1862, 5, 246) through sulphuric acid.

2. By the action of alkali hypochlorite,  $\text{OCI}'$ , or bleaching powder solution on excess of aqueous ammonia (Marchand, 1844; Kolb, *Ann. Chim. Phys.* 1867, [iv], 12, 266):

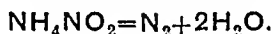


(With bleaching powder explosion may result, though this is unusual.)

3. By the action of bromine water or alkali hypobromite solution on ammonia, the reactions being similar to those in (1) and (2). By using bromine, and drying with phosphorus pentoxide in an all-glass apparatus, pure nitrogen may be obtained (Waran, *Phil. Mag.* 1921, [vi], 42, 246).

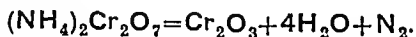
4. Instead of oxidising the ammonia, the pure gas may be decomposed by passing over nickel powder at  $1,000^\circ$  in a quartz tube, the residual ammonia frozen out in liquid air and the nitrogen separated from the hydrogen by freezing out solid nitrogen by cooling with evaporating liquid air, the hydrogen retained in the solid being removed by exhaustion (Harteck, *Ber.* 1930, 63 [B], 427).

5. By heating a solution of ammonium nitrite, or of sodium nitrite and ammonium chlorido (Corenwinder, *Ann. Chim. Phys.* 1849, [iii], 26, 296):



The reaction seems to involve free nitrous acid, since it is inhibited by ammonia (Arndt, *Z. physikal. Chem.* 1901, 39, 64; 1903, 45, 571). The gas may contain a little nitric oxide; if this is absorbed by ferrous sulphate solution it is evolved again on shaking, whilst with permanganate solution oxygen is liberated in varying amounts. The best procedure (Gibbs, *Ber.* 1877, 10, 1387; Knorre, *Chem. Ind.* 1902, 25, 531) is to warm a solution of 1 part of sodium nitrite, 1-2 parts of ammonium sulphate, and 1 part of potassium dichromate, and wash the gas with a solution of 5 vol. of saturated potassium dichromate solution and 1 vol. of concentrated sulphuric acid.

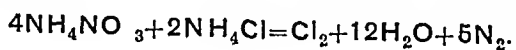
6. By heating ammonium dichromate, or a mixture of ammonium chlorido and potassium dichromate:



The reaction is violent and the nitrogen is not quite pure.

7. By heating glycerol (2 parts) and  $\text{NH}_4\text{NO}_3$  (1 part) (Mai, *Ber.* 1901, 34, 3805). The reaction begins at  $190^\circ$ , but once initiated proceeds at  $160$ – $170^\circ$  without further heating until the temperature has fallen to  $150^\circ$ . A few drops of sulphuric acid cause the reaction to proceed more regularly and at a lower temperature. Carbon dioxide is present in small quantity. The yield of nitrogen is nearly theoretical.

8. By heating a mixture of dry ammonium nitrate and ammonium chloride and absorbing the chlorine from the gas by passing through alkali:

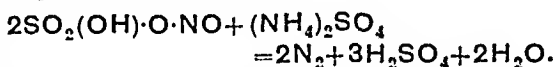


9. By passing a mixture of (a) nitric oxide or (b) nitrous oxide with ammonia over heated copper gauze or platinised asbestos. If nitrous oxide is used precautions must be taken to prevent explosions. The nitrogen is purified by passing through dilute sulphuric acid, over fused potassium hydroxide, through concentrated sulphuric acid, and finally over red-hot copper gauze (Baxter and Hickey, *Amer. Chem. J.* 1905, 33, 300).

10. The action of zinc on fused ammonium nitrate.

11. The thermal decomposition of sodium azide,  $\text{NaN}_3$ , or barium azide,  $\text{Ba}(\text{N}_3)_2$ , in an evacuated apparatus. This gives very pure nitrogen, but there is danger of explosion (Tiede, *Ber.* 1916, 49, 1742; Justi, *Ann. Physik*, 1931, 10, 983).

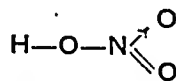
12. Heating nitrososulphuric acid with ammonium sulphate at  $130^\circ$  (Pelouze, *Ann. Chim. Phys.* 1841, [iii], 2, 47):



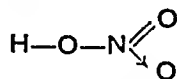
Compressed nitrogen is sold in grey cylinders; it contains a little oxygen, which may be removed by passing the gas slowly over a long length of clean copper turnings heated to bright redness, or through alkaline pyrogallol solution.

#### PHYSICAL PROPERTIES OF NITROGEN.

Nitrogen is a colourless, odourless, tasteless, neutral gas, sparingly soluble in water and a non-supporter of combustion. The normal valency of nitrogen is 3 and the molecule  $\text{N}_2$  contains a triple bond of three shared electron pairs  $\text{N}\equiv\text{N}$  or  $:\text{N}:::\text{N}:$  (Pauling, *J. Amer. Chem. Soc.* 1932, 54, 3570; Petrikaln, *Z. physikal. Chem.* 1929, B, 3, 360). The maximum covalency of nitrogen is 4, the compounds formerly considered to contain 5-valent nitrogen (ammonium salts, diazonium salts, nitro-compounds, and nitrates, etc.) having either one electrovalent bond, e.g.,  $[\text{NH}_4]^+\text{Cl}^-$ , when the four valencies are arranged tetrahedrally (Mills and Warren, *J.C.S.* 1925, 127, 2507), or else one co-ordinate bond, e.g., in nitric acid,



in resonance with



the two  $\text{N}-\text{O}$  bonds being statistically identical (Pauling and Brockway, *J. Amer. Chem. Soc.* 1937, 59, 13). The tetrahedral arrangement for 3- as well as 4-valent nitrogen is confirmed by the infra-red absorption spectrum of ammonia (Robertson and Fox, *Proc. Roy. Soc.* 1928, A, 120, 161) and also follows from wave-mechanical calculations (Pauling, *Physical Rev.* 1931, [ii], 37, 1185; *J. Amer. Chem. Soc.* 1931, 53, 1379). The radius of the nitrogen atom is 0.71 Å. (Goldschmidt, *Skr. Akad. Oslo*, 1926, No. 1, paper 2, p. 27; Vegard and Berge, *ibid.* 1926, No. 2, paper 10); that of the molecule  $\text{N}_2$  on

the assumption of an elastic sphere is about 1.5 Å. (Chapman, Phil. Trans. 1912, A, 211, 433). The moment of inertia of  $N_2$  is  $13.85 \times 10^{-40}$  g.-cm.<sup>2</sup> (Rasetti, Nuovo Cim. 1929, 6, 356; Physical Rev. 1929, [ii], 34, 367); the internuclear distance is 1.10 Å. (Vegard, Z. Physik, 1929, 58, 497).

Although the nitrogen molecule should exist in *ortho*- and *para*-states (v. HYDROGEN, Vol. VI, 321d), these have not been detected (Hartack and Schmidt, Naturwiss. 1930, 18, 282, contradicting Justi, *ibid.*, p. 227). The heat of dissociation of the molecule into normal atoms ( $N_2=2N$ ) is 169.3 kg.-cal. per g.-mol. and is much smaller than was formerly supposed (Herzberg and Sponer, Z. physikal. Chem. 1934, B, 26, 1; Van der Ziel, Physica, 1937, 4, 373; for later arguments for a higher value, 212.3 kg.-cal. per g.-mol., see Hagstrum and Tate, Physical Rev. 1941, [iii], 59, 354; Gaydon, Nature, 1944, 153, 407; Gaydon and Penney, Proc. Roy. Soc. 1945, A, 183, 374). The stable isotopes of nitrogen are of masses 14 and 15 (Naudé, Physical Rev. 1929, [iii], 34, 1498; 1930, [ii], 35, 130; 36, 333; Herzberg, Z. physikal. Chem. 1930, B, 9, 43) with the relative abundance  $^{14}N:^{15}N=346:1$  (Murphy and Urey, Physical Rev. 1932, [ii], 41, 141). Unstable radioactive isotopes,  $^{13}N$  and  $^{16}N$ , are formed artificially, e.g., by bombarding carbon with deuterons:  $^{12}C+^2H=^{13}N+^1_0n$  (Joliot and Curie, Nature, 1934, 133, 202; Henderson, Livingstone, and Lawrence, Physical Rev. 1934, [ii], 45, 428; Seaborg, Chem. Reviews, 1940, 27, 199).

The isotope  $^{15}N$  was detected by mass spectrograph and optical absorption spectrum methods (Naudé, *l.c.*). By using the exchange reaction between ammonium sulphate and ammonia gas, Urey, Fox, Huffman, and Thode (J. Amer. Chem. Soc. 1937, 59, 1407; cf. Schoenheimer, Rittenberg, Fox, Keston, and Ratner, *ibid.*, p. 1768) have concentrated the heavier isotope. A solution of ammonium sulphate was pumped to the top of a fractionating column under low pressure, ammonia was liberated from the salt at the foot of the column by addition of caustic soda, and the ammonia gas stripped by a packed column. This ammonia was fed back to the base of the column and escaped at the top. As a result of a 13-day run nitrogen containing 2.54% of  $^{15}N$  was obtained, an increase of concentration of 6.5-fold.

From a critical survey of recent measurements Moles (Z. anorg. Chem. 1927, 167, 46) calculated the normal density of nitrogen gas (wt. of 1 l. at S.T.P. at sea-level and latitude 45°) as  $1.25046 \pm 0.00005$  g. per l. (which is distinctly smaller than the best earlier values, giving 1.2507 g. per l. in good agreement), and with the compressibility coefficient  $\lambda=0.000424$  in  $1+\lambda=(pv)_0/(pv)$ , this gives from the limiting density the atomic weight  $N=14.0082$ , in agreement with the chemical value (Hönigschmid, Zintl, and Thilo, *ibid.* 1927, 163, 65; Baxter and Greene, J. Amer. Chem. Soc. 1931, 53, 604). The density at S.T.P. is 0.05% greater than the limiting density (ideal gas); the density of atmospheric nitrogen containing inert gases is 0.5% higher than that of pure nitrogen

(Rayleigh and Ramsay, Phil. Trans. 1895, 186, 187). Densities of pure nitrogen gas at 0°C. at higher pressures (taking 1.2507 g. per l. at S.T.P.) are (Bartlett, J. Amer. Chem. Soc. 1927, 49, 687, 1955):

$p$ atm.	1	50	100	200	300
$p$ g. per litre.	1.2507	63.513	127.03	240.70	329.71
$p$ atm.	400	600	800	1,000	
$p$ g. per litre.	397.39	491.98	555.21	604.37	

The compressibility of nitrogen (giving the deviations from Boyle's law) has been determined up to high pressures (Amagat, Ann. Chim. 1893, [vi], 29, 68; Onnes and van Urk, Comm. Leiden, 1924, 169d; Millar and Sullivan, Techn. Papers U.S. Bur. Mines, 1928, No. 424; Bartlett, Cupples, and Tremearne, J. Amer. Chem. Soc. 1928, 50, 1275; Smith and Taylor, *ibid.* 1923, 45, 2107; 1926, 48, 3122; Heuse and Otto, Ann. Physik, 1929, 2, 1012; Keyes, Smith, and Joubert, J. Math. Phys. Mass. Inst. Tech. 1922, 1, 191; Kvalnes and Gaddy, J. Amer. Chem. Soc. 1931, 53, 395; Benedict, *ibid.* 1937, 59, 2224, 2233; Deming and Shupe, *ibid.* 1930, 52, 1382; Physical Rev. 1931, [ii], 37, 638; 1934, [ii], 45, 109; Maron and Turnbull, Ind. Eng. Chem. 1941, 33, 69, 246, 408; J. Amer. Chem. Soc. 1942, 64, 44), and compressibilities of binary and ternary mixtures of nitrogen, hydrogen, and methane by Kritschewsky and Levchenko (Acta Physicochim. U.R.S.S. 1941, 14, 271). The product  $pv$ , as with all gases, increases at high pressures; if the value at S.T.P. is taken as 1, Bartlett gives the following values for nitrogen at 20°C.:

$p$ atm.	50	100	200	400
$pv$	1.0667	1.0745	1.1320	1.3467
$p$ atm.	500	600	800	1,000
$pv$	1.4761	1.6098	1.8817	2.1481

Some values at very high pressures found by Bridgman (Proc. Amer. Acad. 1924, 59, 171) are, at 68°C. ( $pv=1$  at 0°C. and 1 kg. per sq. cm.):

$p$ kg. per sq. cm.	4,000	6,000	8,000
$pv$	5.82	7.95	9.94
$p$ kg. per sq. cm.	10,000	13,000	15,000
$pv$	11.91	14.70	16.50

The thermodynamic properties of oxygen-nitrogen mixtures are given by Kritschewsky and Tonotscheschnikow (Z. physikal. Chem. 1936, 176, 338).

The coefficient of expansion  $\alpha$  and of pressure  $\beta$ , and their dependence on temperature and pressure, have been measured for nitrogen gas over a wide range (Chappuis, etc., Trav. Mém. Bur. internat. 1902, 12; 1907, 13; Jaquero and Perrot, Compt. rend. 1904, 138, 1032; Burgess, J. Chim. phys. 1913, 11, 529; Henning, Otto, and Holborn, Z. Physik, 1921, 5, 264, 285; 1922, 10, 367; 1924, 23, 77; 30, 320; Ann. Physik, 1929, 2, 1012; Verschoyle, Proc. Roy. Soc. 1926, A, 111, 552); the coefficient of expansion of the liquid is about 0.0055 (Erdmann, Ber. 1906, 39, 1207; Bakker, Z. physikal. Chem. 1914, 86, 160; Thatte, Phil. Mag. 1929, [vii], 7, 887).

The coefficient of expansion increases with increase of pressure to a maximum and then



decreases; the mean values in the range 0–100°C. are:

$p$ atm. . . . .	1	50	200	500	1,000
$(\alpha-1)\times 10^5$ . . .	368	400	433	315	200

The *inversion temperature* for the Joule-Thomson effect for nitrogen varies from 243° for 159 kg. per sq. cm. to 163° for 30 kg. per sq. cm. for expansion to 1 atm. pressure (Olszewski, Bull. Acad. Polonaise, 1906, 792; Phil. Mag. 1907, [vi], 13, 722; Porter, *ibid.* 1910, [vi], 19, 888).

The *viscosity*  $\eta$  of nitrogen gas is  $1.728\times 10^{-4}$  dyne-sec. per sq. cm. at 16.1°C. and  $2.461\times 10^{-4}$  at 200°; the *Sutherland constant*  $C$  is 102.7 (Trautz and Baumann, Ann. Physik, 1929, 2, 133; cf. Markowski, *ibid.* 1904, 14, 742; at higher temperatures, Trautz and Zink, *ibid.* 1930, 7, 427; at higher pressures, Michels and Gibson, Proc. Roy. Soc. 1931, A, 134, 288). The viscosity of the liquid at the boiling-point is about  $16\times 10^{-4}$ .

The *dielectric constant* of nitrogen gas at S.T.P. is 1.0005824 (Michels, Jaspers, and Sanders, Physica, 1934, 1, 627; Zahn, Physical Rev. 1924, [ii], 24, 400; effect of temperature and pressure, Uhlig, Kirkwood, and Keyes, J. Chem. Physics, 1933, 1, 155); that of liquid nitrogen is 1.58 (Wachsmuth and Messtorff, Verh. phys. Ges. 1922, 3, 7), and that of the solid 1.515 (McLennan, Jacobsen, and Wilhelm, Trans. Roy. Soc. Canada, 1930, 24, III, 40). The *dipole moment* of the gas is zero, and the *specific magnetic susceptibility* is  $\chi.10^6=-0.430$  at room temperature (Havens, Physical Rev. 1933, [ii], 43, 992).

The *refractive index* of the gas for  $\lambda=5,460$  Å. is  $1+299.7\times 10^{-6}$  at S.T.P. (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1910, A, 83, 149; Phil. Mag. 1913, [vi], 25, 592; cf. Ramsay and Travers, Z. physikal. Chem. 1898, 25, 100; Jones and Partington, Phil. Mag. 1915, [vi], 29, 28). The refractive index of the liquid at  $-190^\circ$  for the  $D$ -line is 1.2053 (Liveing and Dewar, *ibid.* 1893, [v], 36, 328). On the *dispersion* of nitrogen, see Gerald, Ann. Physik, 1921, 65, 82; Korff and Breit, Rev. Mod. Physics, 1932, 4, 471).

The *thermal conductivity* of the gas at S.T.P. is  $k=5.5\times 10^{-5}$  g.-cal. per cm. per sec. per degree (Ibbs and Hirst, Proc. Roy. Soc. 1929, A, 123, 134) and the thermal coefficient of the conductivity is  $(k_t-k_0)/k_0=0.0029$  (Dickins, *ibid.* 1934, A, 143, 517).

The *specific heats* of the gas at constant volume  $c_v$  and at constant pressure  $c_p$  and the ratio  $c_p/c_v$  are discussed by Partington and Shilling ("The Specific Heats of Gases," Benn Bros., 1924, p. 204; Phil. Mag. 1928, [viii], 6, 926; Trans. Faraday Soc. 1926, 22, 277; Partington and Howe, Proc. Roy. Soc. 1924, A, 105, 225; Dixon and Greenwood, *ibid.*, p. 199). The values in g.-cal per g.-mol per degree are:

$t^\circ\text{C.}$	0	100	200	400	600	800	1,000
$C_p$ .	6.92	6.94	6.97	7.05	7.13	7.20	7.30
$C_v$ .	4.92	4.95	4.99	5.06	5.14	5.22	5.32

Numerous formulæ have been proposed to represent the effect of temperature on the specific heats, e.g.,  $c_p=0.2491+9.5\times 10^{-6}t$  g.-cal. per g.; and from 300–3,000°K. ( $T$ ) (Kelley, U.S.

Bur. Mines Bull. 1934, No. 371; J. R. Partington, "Chemical Thermodynamics," Constable, 1940, p. 215):  $C_p=6.50+1.00\times 10^{-3}T$ . The specific heats of the solid and liquid at low temperatures (there is a transition in the solid at 35.6°K.) (Clusius, Z. physikal. Chem. 1929, B, 3, 41; Giauque and Clayton, J. Amer. Chem. Soc. 1933, 55, 4875; Wiebe and Brevoort, *ibid.* 1930, 52, 622; older values in Alt, Ann. Physik, 1904, 13, 1010) are:

$T^\circ\text{abs.}$ . . .	10	20	30	50	70
$C_p$ solid . . .	1.2	4.6	8.0	10.0	1.35 (liq.)

From these and other values the *entropy* and *free energy* of the gas have been calculated for various temperatures (Giauque and Clayton, *l.c.*).

The *critical constants* of nitrogen are (Pickering, J. Physical Chem. 1924, 28, 97; Sci. Papers U.S. Bur. Stand. 1926, 21, 597);  $t_c=-147.1^\circ\text{C.}$ ,  $p_c=33.5$  atm., critical density 0.311 g. per ml. (for earlier values, see Wroblewski, Compt. rend. 1885, 100, 979; Dewar, Proc. Roy. Soc. 1904, 73, 251; Crommelin, Proc. K. Akad. Wetensch. Amsterdam, 1915, 17, 959).

The *boiling-point* is  $-195.8^\circ\text{C.}$  (Giauque and Clayton, J. Amer. Chem. Soc. 1933, 55, 4875; for earlier values, see Dewar, Proc. Roy. Soc. 1902, A, 69, 360 ( $-195.0^\circ$ ); Grunmach, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1906, 679 ( $-195.9^\circ$ ); Alt, Ann. Physik, 1906, 19, 739 ( $-195.55^\circ$ ); Henning and Heuse, Z. Physik, 1924, 23, 105).

The *vapour pressures* in atm. of liquid nitrogen at various absolute temperatures  $T$ , and also the boiling-points under various pressures in atm., are accurately produced by the formula  $\log p=-304.494/T+3.93352$  (Dodge and Davis, J. Amer. Chem. Soc. 1927, 49, 610; for older values, see Olszewski, Compt. rend. 1884, 99, 133; Baly, Phil. Mag. 1900, [v], 49, 517; Fischer and Alt, Sitzungsber. K. Akad. München, 1902, 113). Vapour pressures of nitrogen isotopes are discussed by Kishenbaum and Urey (J. Chem. Physics, 1942, 10, 706, 710). The *latent heat of evaporation*,  $l_e$ , at the boiling-point is 47.58 g.-cal. per g. (Giauque and Clayton, J. Amer. Chem. Soc. 1933, 55, 4875; cf. Dewar, Proc. Roy. Soc. 1905, 76, 325; Alt, *l.c.*). Some values of the vapour pressures and latent heats at various temperatures (cf. Wiebe and Brevoort, *l.c.*) are:

$t^\circ\text{C.}$ . . . . .	-213	-203	-193	-183
$p$ kg. per sq. cm. .	0.06*	0.4	1.37	3.6
$l_e$ g.-cal. per g. .	52	50	47	43

$t^\circ\text{C.}$ . . . . .	-173	-163	-153
$p$ kg. per sq. cm. .	7.7	14	25
$l_e$ g.-cal. per g. .	39	33	22

\* Solid.

The *compressibility* of liquid nitrogen ( $-198^\circ$ , to 240 atm.) is  $250\times 10^{-6}$  atm. $^{-1}$  (Simon and Kippert, Z. physikal. Chem. 1927, 135, 113).

The *surface tension*,  $\gamma$ , of the liquid at the boiling-point is 8.7 dynes per cm. (Verschaffelt, 1925, quoted in Landolt-Börnstein, "Physikalisch-chemische Tabellen," Berlin, 1931, Ergzb. II, i, p. 166; Grunmach, Ann. Physik, 1907, 22, 107); the dependence of  $\gamma$  on absolute temperature is given by  $\gamma=\gamma_0(1-T/T_c)^n$  where  $T_c$ =critical temperature (abs.) and  $n$  is

There has been considerable discussion about the nature of active nitrogen, and although the problem has been greatly clarified in recent years there are still some obscure features (for summary, see S. K. Mitra, "Active Nitrogen, A New Theory," Calcutta, 1945). It was considered probable that the activity is not associated with any ionised form of nitrogen, since it is unaffected by the removal of ions from the gas which has been subjected to the discharge, but Mitra (*l.c.*) has proposed the theory that active nitrogen consists of  $N_2^+$  ions. Rayleigh suggested that active nitrogen contains uncharged nitrogen atoms, and this has been largely substantiated. The suggestion by Trautz (Z. Elektrochem. 1919, 25, 297) that it is triatomic nitrogen,  $N_3$ , probably not a cyclic molecule because of the nitride formation and the absence of azide formation (azides being then thought to have a cyclic structure), is no longer entertained, since Rayleigh was unable to condense any form of active nitrogen by strong cooling. The spectroscopic evidence, on the other hand, indicates that the  $\alpha$ -bands or First Positive bands are due to the uncharged nitrogen molecule and Dhar (Z. anorg. Chem. 1924, 141, 1; 1926, 159, 103; J. Physical Chem. 1924, 28, 948) suggested that nitrogen molecules are excited by the discharge and afterwards give up their energy with the emission of the glow. Duffieux (Nature, 1926, 117, 302) considered that the excitation is produced by ionised atoms, the Second Positive band group (which predominates in the discharge during the activation of the nitrogen) being due to the atom.

The spectroscopic evidence points to the emission of the glow by the diatomic molecule  $N_2$  in some peculiar state, and Birge (*ibid.* 1924, 114, 642; Physical Rev. 1924, [ii], 23, 294) and Saha and Sur (Phil. Mag. 1924, 48, 421; review by Saha and Mathur, Proc. Nat. Acad. Sci. India, 1936, 6, 120) considered that this is the metastable excited neutral molecule  $N_2$ .

Wiley and Rideal (J.C.S. 1926, 1804) found the value 42,500 g.-cal. for the heat of formation of active nitrogen by allowing it to react with nitric oxide. Wiley (*ibid.* 1927, 2831; Nature, 1927, 119, 924) at first supposed that the glow and chemical activity are independent, and that different stages in activity are possible. Rayleigh also thought the glow could be destroyed without destroying the chemical activity. It was thus considered possible that the average energy of chemically active nitrogen might be appreciably smaller than that of the glowing molecules, and that the glowing nitrogen is only a fraction of the total chemically active nitrogen and is in a considerably more excited state than the average. This was supposed to clear up a discrepancy thought to exist between the observed heat of formation (*see above*) and the heat of dissociation of the nitrogen molecule into atoms. The more recent considerable reduction in the latter value has modified this argument, and in later work Wiley (J.C.S. 1930, 339) concluded that the glow and chemical phenomena are not completely independent.

When Herzberg and Sponer (Z. physikal. Chem. 1934, B, 26, 1) showed that the heat of dissociation  $N_2 = 2N$  is 169.3 kg.-cal. per g.-mol.,

much smaller than was previously assumed (but *see above*, p. 506a), it was possible for Cario (Z. Physik, 1934, 89, 523) to present a consistent scheme for the mechanism of glow production. In this, metastable  $N_2$  molecules with 6.14 v. (instead of 8.1 v., as previously assumed) are supposed to be excited by collision with metastable N atoms with energies of 3.56 v. ( $^2P$  state) and 2.37 v. ( $^2D$  state), and the resulting  $N_2$  molecule, with energy 9.70 or 8.51 v., then emits radiation. The chemical activity is supposed to be due to the atomic forms.

The foreign gases necessary for the production of the glow act catalytically, since they play no part in the actual light emission. Rayleigh showed that the decay of the glow is influenced by the walls of the vessel, and Bonhoeffer and Kaminsky (Z. physikal. Chem. 1927, 127, 385) found that the effects of different gases markedly depend on the walls. Lewis (J. Amer. Chem. Soc. 1929, 51, 654, 665) showed that baking the surface causes the afterglow to disappear, but that the glow can be made to reappear on the addition of sufficient water vapour to cover the surface. Willey (J.C.S. 1928, 1620; 1930, 336, 1146; cf. Sponer, Z. Physik, 1925, 34, 622; Herzberg, *ibid.* 1928, 46, 878) examined the effect of other foreign gases and of the walls on the decay of the glow, and Rayleigh (Proc. Roy. Soc. 1935, A, 151, 567) by coating the walls with phosphoric acid was able to prolong the glow period very considerably. All these results show that the glow occurs in the gas, that it is due to a change which can occur on very clean walls without glow, and that the function of the traces of foreign gases necessary for the production of the glow is probably to "poison" the catalysing walls by covering them with an adsorbed film and so forcing the change into the gas phase, where it occurs, probably as a result of termolecular collisions between excited atoms and molecules, with the emission of the glow.

Later investigations by Rayleigh have reopened some puzzling questions as to the nature of active nitrogen. He showed (*ibid.* 1942, A, 180, 123) that the effect of oxygen is to produce some modification of the walls of a glass vessel which is favourable to the production of active nitrogen. Strong preliminary heating of the walls, or even heating in nitrogen at atmospheric pressure, brings about inhibition of the after-glow, whilst heating in oxygen at 1 mm. pressure restores its formation. He concluded (*ibid.* 1942, A, 180, 140) that ionisation of the  $N_2$  molecule, with the energy 15.51 v., is closely associated with the formation of active nitrogen (*cf.* Mitra, *l.c.*). The ionisation and glow mechanisms are probably different, but the energy (about 9.6 v.: *see above*) attributed to active nitrogen on spectroscopic grounds is regarded with suspicion; too much stress has perhaps been laid on the spectroscopic aspect, since the ionisation may involve as many atoms as are concerned in the light emission. Rayleigh (*ibid.* 1940, A, 176, 1) found that if a volume of glowing nitrogen is doubled by diffusion into ordinary nitrogen, the glow intensity is reduced 4.3-fold, or about 4-fold, as would be expected if the reaction were bimolecular as regards active

nitrogen (*see above*). On compression with a solid piston, the brightness varied inversely as the cube of the volume, and over the range examined it varied as  $T^{-0.64}$ , where  $T$  is the absolute temperature, whilst in most ordinary chemical reactions the effect is proportional to about  $T^{+1.00}$ . The most striking results are those (*ibid.* 1940, A, 176, 16) in which pieces of gold, silver, copper, or platinum were made red-hot, and even melted, when exposed to active nitrogen formed in a low-pressure discharge, without any chemical effect on the metal. The energy collected and liberated by the metal is surprisingly large and cannot be reconciled with existing theories of active nitrogen; only with difficulty, in fact, with the assumption of complete dissociation of nitrogen molecules. The energy radiated in the after-glow amounts to only about one thousand of that collected by the metals, so that the luminosity is of quite subordinate importance from the point of view of the energy of the active nitrogen. A large dissipation of energy must occur in some non-luminous effect, the nature of which is obscure, and it is uncertain at what period in the decay time it is mainly released. Kaplan (*Physical Rev.* 1940, [ii], 57, 662; *cf.* Kamiyama and Sugiura, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1939, 36, Abstr., 52; 1940, 37, 479) found that the character of the glow changed with time, the line 3,467A having a greater relative intensity as compared with the Second Positive band system (p. 508c) later in the life of the glow.

The problem of active nitrogen is still far from a satisfactory solution, but most of the experimental work so far available points to the nitrogen atom, whether in normal or excited states, as the probable carrier of the chemical activity.

The strong green or blue-green fluorescence excited by active nitrogen with many salts (Lewis, *Nature*, 1923, 111, 599) may be due to chemical reaction with active nitrogen or to the presence of free electrons, but is probably a chemiluminescence phenomenon in which the decomposition of the activating substance furnishes the energy for luminescence (Bonhoeffer and Kaminsky, *Z. physikal. Chem.* 1927, 127, 385).

In the explosion of mixtures of carbon monoxide, oxygen, and nitrogen some kind of activation of the nitrogen is supposed to occur (Bone, Newitt, and Townend, *J.C.S.* 1923, 123, 2008; *Proc. Roy. Soc.* 1923, 103, 205; 1924, 105, 406) but the effect was not adequately studied. According to Lowry (*J.C.S.* 1912, 101, 1152; *Trans. Faraday Soc.* 1913, 9, 189) when air is subjected first to a silent discharge (which will form ozone) and then to a spark discharge (which will form nitric oxide), a peculiar form of active nitrogen is formed. The results, however, are probably due to reactions of ozone and nitrogen oxides (Willey and Foord, *J.C.S.* 1932, 153).

#### HALIDES OF NITROGEN.

Nitrogen Fluoride, obtained by electrolysis fused anhydrous ammonium hydrogen fluoride (Ruff, Fischer, and Luft, *Z. anorg. Chem.* 1928, 172, 417), is a colourless gas at ordinary

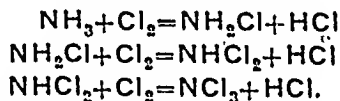
temperatures, and analysis and density measurements give the formula  $\text{NF}_3$ . It is condensed by liquid air to a colourless mobile liquid, b.p.  $-119^\circ$ , freezing somewhat above  $-216.6^\circ$  (Ruff and Clusius, *Z. anorg. Chem.* 1930, 190, 267). It is insoluble in water and unattacked by hydrogen, but when sparks are passed through a mixture of the gas with water vapour, hydrogen fluoride and oxides of nitrogen are formed. With hydrogen under similar conditions, the reaction is very violent, nitrogen and hydrogen fluoride being formed. There is no reaction with mercury, manganese dioxide, potassium hydroxide solution, or glass at the ordinary temperature. The toxic properties of  $\text{NF}_3$  are due to its inhibiting the oxidation of haemoglobin in the blood.

Ruff and co-workers (*ibid.* 1931, 198, 32) claim to have isolated several intermediate compounds in the preparation of  $\text{NF}_3$ , including  $\text{NH}_2\text{F}$ ,  $\text{NHF}_2$ , and a yellow compound thought to be  $\text{NF}_2$ , all gases at ordinary temperature and pressure.

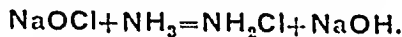
Under all conditions, nitrogen trifluoride and other nitrogen fluorides are produced in addition to nitrogen by the action of fluorine on ammonia (Ruff and Hanke, *ibid.* 1931, 197, 273, 395).

Nitrogen trifluoride may be analysed by (a) the reaction with heated hydriodic acid:  $\text{NF}_3 + 7\text{HI} = \text{NH}_4\text{I} + 3\text{HF} + 3\text{I}_2$ , the iodine being titrated, (b) the reaction with sodium:  $2\text{NF}_3 + 6\text{Na} = \text{N}_2 + 6\text{NaF}$  (Ruff *et al.*, *ibid.* 1931, 197, 273; 1931, 198, 32).

Nitrogen Chlorides.—By the action of chlorine on ammonia under suitable conditions, three substitution products are formed (with ammonia in excess, only nitrogen is obtained, p. 504d):



Monochloroamine,  $\text{NH}_2\text{Cl}$ , is formed in solution by the action of ammonia on chlorine water, and is used in sterilising water supplies, acting more powerfully than chlorine. It is also formed from sodium hypochlorite solution and a slight excess of ammonia (Playfair, *Mem. and Proc. C.S.* 1845, 3, 356; F. Raschig, *Ber.* 1907, 40, 4586; "Schwefel- und Stickstoffstudien," Verlag Chemie, 1924, p. 50):

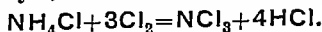


By distilling the solution in vacuum, drying the vapour with anhydrous potassium carbonate, and condensing it in liquid air, colourless crystals of pure  $\text{NH}_2\text{Cl}$  are obtained, melting at  $-66^\circ$  and decomposing explosively at  $-50^\circ$  into nitrogen, chlorine, and ammonium chloride (Marckwald and Wille, *Ber.* 1923, 56 [B], 1319).

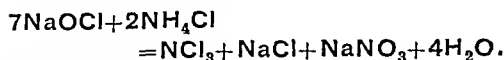
Dichloroamine,  $\text{NHCl}_2$ , is less stable than monochloroamine and is known only in solution; it is formed by acidifying a solution of  $\text{NH}_2\text{Cl}$  or by the action of chlorine on excess of ammonium sulphate solution buffered to pH 4.5–5.0 (Chapin, *J. Amer. Chem. Soc.* 1929, 51, 2112).

Trichloroamine or Nitrogen Trichloride,  $\text{NCl}_3$ , was accidentally obtained by Dulong (who sustained serious injury by an explosion) in 1811 by the action of chlorine on a solution of am-

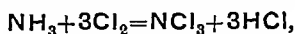
monium chloride (Schweigger's J. 1813, 8, 302; Ampère, Ann. Chim. Phys. 1885, [vi], 4, 12; Victor Meyer, Ber. 1888, 21, 26):



Balard (Ann. Chim. Phys. 1834, [ii], 57, 259) obtained it by the action of hypochlorous acid on ammonium chloride (ammonium sulphate is preferable), and Hentschel (Ber. 1897, 30, 1434, 1792) by the action of sodium hypochlorite on ammonium chloride:



Nitrogen chloride is also formed by the action of excess of chlorine on ammonia, a reaction formerly thought to involve the intermediate formation of ammonium hypochlorite; since it occurs between anhydrous ammonia and chlorine this cannot be true, and probably a simple substitution reaction occurs:



followed by  $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$  (Noyes and Lyon, J. Amer. Chem. Soc. 1901, 23, 460; Noyes and Haw, *ibid.* 1920, 42, 2167; Bray and Dowell, *ibid.* 1917, 39, 905).

Nitrogen trichloride is also formed at the anode in the electrolysis of concentrated ammonium chloride solution (Kolbe, J. pr. Chem. 1847, [i], 41, 137; Hofar, Chem.-Ztg. 1896, 20, 478).

By adding a calcium hypochlorite solution acidified with hydrochloric acid to ammonium chloride solution, and shaking with benzene, the  $\text{NCl}_3$  formed is dissolved in the benzene (Hentschel, Ber. 1897, 30, 1434, 1792, 2642). According to Rai (Chem. News, 1918, 117, 253) it can be prepared by the action of bleaching powder on a saturated solution of ammonium chloride at about  $0^\circ$ , without the use of hydrochloric acid or a solvent such as benzene or carbon tetrachloride.

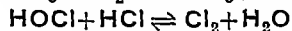
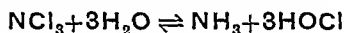
By covering 150 ml. of carbon tetrachloride with a concentrated aqueous solution of ammonium chloride, passing in chlorine gas with vigorous shaking, and then washing with water, a bright yellow solution of nitrogen trichloride is obtained (Chapman and Vodden, J.C.S. 1909, 95, 138).

Nitrogen trichloride is a yellowish, volatile, very pungent-smelling oil, the vapour of which strongly attacks the eyes and mucous membrane;  $\rho$  1.653, b.p.  $71^\circ$ . It detonates at  $93^\circ$ , or in contact with organic matter, phosphorus, arsenic, ozone, or alkalis. Metals, strong acids, resins and sugar do not cause its explosion, which is, however, brought about by exposure to strong light (Porret, Wilson, and Kirk, Ann. Phys. Chem. 1814, [i], 47, 56). It is strongly endothermic, the heat of formation being  $-38,477$  g.-cal. (Deville and Hautefeuille, Compt. rend. 1869, 69, 152; Deville and Troost, *ibid.*, p. 204). It reacts slowly with dilute ammonium chloride solution and more rapidly with a concentrated solution:  $\text{NCl}_3 + \text{NH}_4\text{Cl} = \text{N}_2 + 4\text{HCl}$ , and is decomposed by ammonia and ammonium sulphide solutions. Dry hydrogen chloride converts it quantitatively into ammonium chloride (Noyes).

Nitrogen trichloride dissolves in benzene, ether, chloroform, carbon tetrachloride, and carbon disulphide. The benzene solution has been used for chlorinating organic substances (Hentschel, Ber. 1897, 30, 2642).

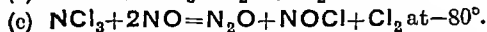
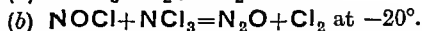
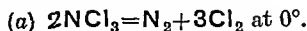
The formula  $\text{NCl}_3$  was assigned to nitrogen chloride by Dulong (Schweigger's J. 1813, 8, 302), Bineau (Ann. Chim. Phys. 1845, [iii], 15, 82), and Deville and Hautefeuille (Compt. rend. 1869, 69, 152). Davy (Phil. Trans. 1813, 103, I, 242) found the chlorine to be in excess of that required for this formula and suggested  $\text{NCl}_4$ . Porret, Wilson, and Kirk (*l.c.*), and Gladstone (J.C.S. 1854, 7, 51) concluded that hydrogen was present (the latter giving the formula as  $\text{N}_2\text{HCl}_5$ ), but the methods of analysis were not accurate. Gattermann (Ber. 1888, 21, 751; cf. Hentschel, *ibid.* 1897, 30, 1792) determined the chlorine directly by decomposing a weighed quantity of the carefully purified and dried substance with concentrated ammonia, thus forming ammonium chloride, in which the chlorine was estimated as silver chloride, the result closely agreeing with the formula  $\text{NCl}_3$ . This was confirmed by Chapman and Vodden (J.C.S. 1909, 95, 138), who determined the ratio of nitrogen to chlorine, and also proved the absence of hydrogen. Hentschel (*l.c.*) found that with excess of chlorine acting on ammonium chloride the proportion of chlorine in the product can go above  $\text{NCl}_4$ , but this is probably due to dissolved free chlorine.

The hydrolysis of nitrogen trichloride (Seliwanov, Ber. 1894, 27, 1012):

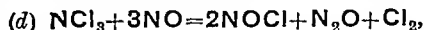


explains the easy reduction to ammonia, and the greater solubility in hydrochloric acid than in sulphuric acid or in water (since hydrochloric acid decomposes hypochlorous acid). Chapman and Vodden (*l.c.*), by shaking a solution of nitrogen chloride in carbon tetrachloride with moderately concentrated hydrochloric acid, removing any nitrogen trichloride from the aqueous solution, and distilling it with alkali, obtained ammonia in quantity.

Nitrogen trichloride is quantitatively reduced to ammonia by sodium sulphite solution (Dowell and Bray, J. Amer. Chem. Soc. 1917, 39, 896). By the interaction of nitrogen trichloride and nitric oxide in a mixed chloroform-carbon tetrachloride solvent three reactions occur (Noyes, *ibid.* 1928, 50, 2902):



Reaction (b) is a subsidiary reaction which occurs slowly at  $-80^\circ$  and is accompanied by the decomposition of 25% of the nitrogen trichloride into nitrous oxide and chlorine, and by reaction (a). At  $-150^\circ$  the reaction is:



probably proceeding in four stages. Attempts to carry out the reaction at  $-185^\circ$  and  $-191^\circ$  were not successful (Noyes, *ibid.* 1930, 52, 4298).

Nitrogen trichloride is a powerful inhibitor of the photochemical union of hydrogen and chlorine (Burgess and Chapman, J.C.S. 1906, 89, 1399). The photochemical decomposition of nitrogen trichloride is retarded by the addition of helium, argon, nitrogen, and oxygen, which have specific effects. Mixtures of chlorine and small quantities of nitrogen give pressure increments corresponding with the net reaction  $2\text{NCl}_3 = \text{N}_2 + 3\text{Cl}_2$  (Griffiths and Norrish, Nature, 1931, 127, 14; Proc. Roy. Soc. 1931, 130, 591; cf. Bowen, J.C.S. 1923, 123, 1203).

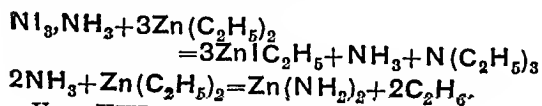
**Nitrogen Bromides.**—The compounds *monobromamine*,  $\text{NH}_2\text{Br}$  (Moldenhauer and Burger, Ber. 1929, 62 [B], 1615) and *dibromamine*,  $\text{NHBr}_2$  (Coleman, *et al.*, J. Amer. Chem. Soc. 1934, 56, 965), are formed by the action of bromine on ammonia, and a red, volatile, explosive oil formed by the action of potassium bromide on nitrogen chloride under water, although not analysed, was supposed to be *nitrogen tribromide* ( $\text{NBr}_3$ ?) (Millon, Ann. Chim. Phys. 1838, [ii], 69, 75).

Nitrogen iodide was first prepared by Courtois (*ibid.* 1813, [i], 88, 304) by digesting powdered iodine with aqueous ammonia. It is also formed as a black precipitate on mixing ammonia and alcoholic iodine solution (Serullas, *ibid.* 1829, [ii], 42, 200; Bunsen, Annalen, 1852, 84, 1):  $5\text{NH}_3 + 3\text{I}_2 = \text{NI}_3 \cdot \text{NH}_3 + 3\text{NH}_4\text{I}$ , or by adding ammonia to a solution of iodine in *aqua regia* or of iodine chloride in potassium iodide solution (Schönbein, J. pr. Chem. 1861, [i], 84, 385), or by mixing solutions of ammonium iodide and bleaching powder (Gladstone, J.C.S. 1855, 7, 51). Nitrogen iodide is usually prepared by gently triturating iodine with concentrated ammonia in a glass mortar, filtering off the black powder and tearing up the moist filter paper and compound, the small portions being allowed to dry on pieces of cardboard at the ordinary temperature. Crystalline nitrogen iodide is best prepared by running a solution of iodine chloride ( $\text{ICl}$ ) in hydrochloric acid into ammonia solution.

Pure nitrogen iodide forms copper-coloured crystals, light-red by transmitted light,  $\rho$  3.5, very readily exploded by shock (even the touch of a feather is often sufficient), warming, or exposure to strong light, especially ultra-violet light; the decomposition reaction is (Eggert, Z. Elektrochem. 1921, 27, 547):  $8\text{NI}_3 \cdot \text{NH}_3 = 5\text{N}_2 + 9\text{I}_2 + 6\text{NH}_4\text{I}$ . It slowly decomposes under water when exposed to light (Guyard, Compt. rend. 1883, 97, 526).

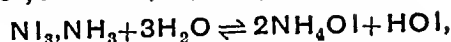
Bunsen's formula for nitrogen iodide  $\text{NI}_3 \cdot \text{NH}_3$ , was confirmed by Chattaway (J.C.S. 1896, 69, 1572; Amer. Chem. J. 1900, 23, 363; 1893, 24, 138, 342). At low temperatures the compounds  $\text{NI}_3 \cdot 2\text{NH}_3$ ,  $\text{NI}_3 \cdot 3\text{NH}_3$  and  $\text{NI}_3 \cdot 12\text{NH}_3$  are formed by the action of ammonia (Hugot, Ann. Chim. Phys. 1900, [vii], 21, 5; Ruff, Ber. 1900, 33, 3025).

The formula  $\text{NI}_3 \cdot \text{NH}_3$  (possibly  $\text{H}_3\text{N} \rightarrow \text{NI}_3$ ) is confirmed by the reaction with zinc ethyl (Silberrad, J.C.S. 1905, 87, 55):

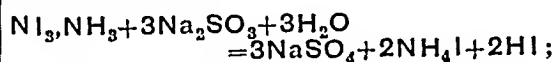


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Nitrogen iodide is hydrolysed as follows (Seliwanov, Ber. 1894, 27, 1012):

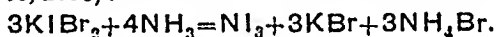


and hypiodous acid is probably involved in its preparation from iodine and ammonia. It is an oxidising agent (Chattaway and Stevens, Amer. Chem. J. 1900, 23, 369) and is reduced, similarly to  $\text{NCl}_3$ , by hydrogen sulphide, sulphur dioxide and sodium sulphite, and arsenious oxide:



hydriodic acid liberates iodine, hydrochloric acid forms iodine chloride, hydrocyanic acid forms iodine cyanide, and alkalis a mixture of iodide and iodate. Each atom of iodine has the oxidising effect of an atom of oxygen, as in hypiodous acid. It reacts with organic iodides (Silberrad and Smart, J.C.S. 1906, 89, 172).

According to F. Raschig ("Schwefel- und Stickstoffstudien," Verlag Chemie, 1924, p. 34)  $\text{NI}_3 \cdot \text{NH}_3$  tends to pass into  $\text{NI}_3$  on washing. *Nitrogen tri-iodide*,  $\text{NI}_3$ , is obtained as a black explosive powder by the action of ammonia gas on solid  $\text{KIBr}_2$  and washing the product rapidly with water (Cremer and Duncanson, J.C.S. 1930, 2750):



#### NITROGEN SULPHIDES, ETC.

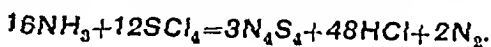
Nitrogen Sulphide was first prepared by Gregory (J. Pharm. Chim. 1835, 21, 315; 1836, 22, 301), but first analysed by Soubeiran (Ann. Chim. Phys. 1838, [ii], 67, 71), who obtained the correct empirical formula  $\text{NS}$ , which was confirmed by Fordos and Gélis (Compt. rend. 1850, 31, 702), who were the first to obtain the pure compound.

Nitrogen sulphide is prepared by passing a rapid current of dry ammonia gas into a 10–15% solution of sulphur chloride,  $\text{S}_2\text{Cl}_2$ , in dry benzene (Francis and Davis, J.C.S. 1901, 85, 259) or dry ether (Valkenburgh and Bailar, J. Amer. Chem. Soc. 1925, 47, 2134) until red fumes appear, after which the liquid is cooled and the current of gas continued for a short time. The ammonium chloride formed is filtered off, and on evaporation of the filtrate orange-red monoclinic crystals (Artini, J.C.S. 1906, 90, 533),  $\rho$  2.2, m.p.  $185^\circ$ , of nitrogen sulphide are obtained, which may be recrystallised from boiling benzene, toluene, or carbon disulphide. It may be sublimed under reduced pressure. It is explosive unless quite pure, when it is fairly stable (Francis and Davis, *loc. cit.*; Schenck, Annalen, 1896, 290, 171). The molecular formula is  $\text{N}_4\text{S}_4$  (Clever and Muthmann, Ber. 1896, 29, 340; Schenck, *loc. cit.*; Francis and Davis, *loc. cit.*). The heat of formation of  $\text{N}_4\text{S}_4$  is  $-127,600$  g.-cal. (Berthelot and Vieille, Compt. rend. 1881, 92, 1307; Ann. Chim. Phys. 1882, [v], 27, 202).

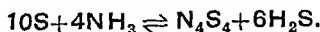
The reaction of formation has been given as:



but Ruff and Geisel (Ber. 1904, 37, 1573) give it as:



Nitrogen sulphide is also formed by the action of sulphur on liquid ammonia in presence of silver iodide (to remove the hydrogen sulphide produced), the reaction being reversible (Moissan, *Compt. rend.* 1901, 132, 510; Ruff and Geisel, *Ber.* 1905, 38, 2659):



Nitrogen sulphide and lead iodide in liquid ammonia give olive-green prisms of lead dithio-di-imide,  $Pb:N_2S_2, 2NH_3$ , and with mercury iodide bright yellow crystals of the mercury thio-di-imide,  $Hg:N_2S, NH_3$ , but in neither case is precipitation complete.

Nitrogen sulphide hydrolyses to form tri- or (probably) penta-thionic acid, sulphur dioxide, and ammonia (Valkenburgh and Bailar, *l.c.*). It reacts with some metal chlorides to form additive compounds (Wölbling, *Z. anorg. Chem.* 1908, 57, 281), with amines (Schenck, *l.c.*), fatty acids, and their anhydrides and halogen derivatives (Francis, *J.C.S.* 1905, 87, 1836), aromatic aldehydes (Davis, *ibid.* p. 1831); with hydrofluoric acid it forms thionyl fluoride (in presence of moisture) (Ruff and Thiel, *Ber.* 1905, 38, 549), and it reacts with dry hydrogen chloride:  $N_4S_4 + 12HCl = 4NH_3 + 4S + 6Cl_2$ . On warming in benzene solution with stannous chloride, nitrogen sulphide forms yellow lustrous leaflets of  $(NSH)_4$ , m.p.  $152^\circ$ , which is not combustible or explosive and evolves ammonia on heating with potassium hydroxide (Wölbling, *l.c.*; Meuwesen, *Ber.* 1929, 62 [B], 1959).

A blue modification of  $N_4S_4$  is obtained by sublimation over silver gauze: it is much less volatile than the common form (Burt, *J.C.S.* 1910, 97, 1171). By subliming  $N_4S_4$  with sulphur at  $128^\circ$  (without silver gauze), a trace of a dark red volatile liquid, with the odour of iodine and freezing to a pale yellow solid at  $-80^\circ$ , is formed: analysis by decomposition gave the formula  $NS_2$  (Usher, *ibid.* 1925, 127, 730).

The structure of  $N_4S_4$  has been the subject of much speculation (Schenck, *l.c.*; Ruff and Geisel, *l.c.*; Arnald *et al.*, *J.C.S.* 1936, 1645); its crystal structure has been determined (Jaeger and Zanstra, *Proc. Acad. Amsterdam*, 1931, 34, 782).

On passing chlorine into a suspension of  $N_4S_4$  in chloroform a tetrachloride  $N_4S_4Cl_4$  is formed, which separates on cooling in splendid yellow crystals, which decompose on heating:  $N_4S_4Cl_4 = 2S_2Cl_2 + 2N_2$ . The substance forms a black tarry mass on exposure to air (Demarçay, *Compt. rend.* 1880, 91, 854; Andereocci, *Atti R. Accad. Lincei*, 1896, 5, 254; *Z. anorg. Chem.* 1897, 14, 246; Muthmann and Seitter, *Ber.* 1897, 30, 627).

The compound  $(SN)_3Cl$  is said to be formed by reaction between the correct amounts of  $N_4S_4$  and  $N_4S_4Cl_4$  in chloroform (Demarçay, *l.c.*). It is, however, probably *thio-trithioazyl chloride*,  $N_3S_4Cl$ , obtained by the action of  $N_4S_4$  on  $S_2Cl_2$  in chloroform solution, or by heating  $N_4S_4$  with acetyl chloride (Muthmann and Seitter, *l.c.*). It is an intensely yellow crystalline powder, which explodes a few minutes after becoming dry. It readily absorbs ammonia.

Thio-trithioazyl chloride is a salt of the radical  $N_3S_4$ ; the *bromide*,  $N_3S_4Br$  (stable in air), *iodide*,  $N_3S_4I$  (very unstable), *thiocyanate*,  $N_3S_4CNS$  (stable in air), and *nitrate*,  $N_3S_4NO_3$ , are known. The nitrate is obtained in sulphur-yellow prisms on evaporating a solution of the chloride in concentrated nitric acid in vacuum. It is very explosive when dry, and the solution in water darkens after a few minutes, giving a black deposit.

Hexasulphamide,  $S_6NH_2$ , is obtained from the mother-liquor resulting from the preparation of  $N_4S_4$  from ammonia and  $S_2Cl_2$  in chloroform (Macheth and Graham, *Proc. Irish Acad.* 1923, 36, 31).

Liquid *nitrogen pentasulphide*,  $N_2S_5$ , is formed by treating 30 g. of  $N_4S_4$  and 500 ml. of pure carbon disulphide in an autoclave at  $100^\circ$  for 2 hours, filtering, distilling off the carbon disulphide, and evaporating at room temperature in vacuum:  $N_4S_4 + 2CS_2 = N_2S_5 + S + 2CNS$ . The residue is triturated with dry ether, and the liquid separated from residual sulphur and cooled at  $-25^\circ$  to separate the remainder of the sulphur. On evaporation of the ether over calcium chloride,  $N_2S_5$  is obtained as a deep red oil, which crystallises from a well-cooled solution in ether in black tablets, m.p.  $-10^\circ$ . It is soluble in most organic solvents and is stable if not exposed to light, but it cannot be distilled (Muthmann and Clever, *Z. anorg. Chem.* 1897, 13, 200).

Nitrogen Selenide,  $N_4Se_4$ , is obtained by passing a rapid stream of dry ammonia gas into a cooled solution of selenium chloride in carbon disulphide (Valkenburgh and Bailar, *J. Amer. Chem. Soc.* 1925, 47, 2134).

#### OXIDES AND OXYACIDS OF NITROGEN.

Nitrous Oxide,  $N_2O$ , was first obtained by Priestley in 1772 ("Experiments and Observations on Air," 1774, Vol. I, pp. 118, 215) by the action of iron or zinc filings, or potassium sulphide or sulphite, on nitric oxide. He called it at first "diminished nitrous air," later *dephlogisticated nitrous air*. Berthollet (*Mem. Acad. Sci. Paris*, 1785 (1788), 316) first obtained it by heating ammonium nitrate, and made a quantitative study of the reaction. The discovery is often credited to the Dutch chemists Deiman, Nieuwland, Bondt, Lauwerenburgh and van Troostwijk, who described it more fully in 1793 (E. Cohen, "Das Lachgas," Leipzig, 1907). It was carefully investigated by H. Davy ("Researches, chiefly concerning Nitrous Oxide," 1800), who determined its composition and discovered its stimulating and anæsthetic physiological properties.

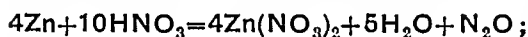
Several attempts have been made to synthesise nitrous oxide from its elements. Matignon (*Compt. rend.* 1912, 154, 203) calculated from Nernst's theorem (J. R. Partington, "Chemical Thermodynamics," Constable, 1940, p. 148) that the direct union of nitrogen and oxygen to *nitrous oxide* should be realisable only at  $3,000^\circ$  under 3,000 atm. pressure. Warburg and Leithauser (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1908, 148) report its formation, with ozone and  $N_2O_5$ , from air in a Siemens' ozoniser, and with  $NO_2$  in a spark discharge between



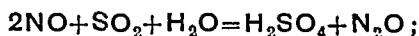
platinum electrodes, but not with a high tension alternating arc, which gives only  $\text{NO}_2$ . Pictet (F.P. 415594, 1910) and Söderman (F.P. 411785, 1910) claim that it is formed in the nitrogen-oxygen flame produced electrically, or by other means, under suitable conditions; the chief product detected spectroscopically or otherwise in a definite part of the flame is said to be  $\text{N}_2\text{O}$ , and by rapid and efficient cooling at this point a yield of 25% of  $\text{N}_2\text{O}$  is claimed. Chapman, Goodman, and Shephard (J.C.S. 1926, 1404) showed that small amounts of nitrous oxide can be formed by passing an electric discharge through nitrogen at low pressure contained in a tube of fused silica, into the walls of which oxygen had previously been driven by passing an electric discharge through that gas contained in the tube at low pressure. No combination between oxygen and nitrogen occurs under the influence of ultra-violet light (Berthelot and Gaudechon, *Compt. rend.* 1910, 150, 1517).

Nitrous oxide may be obtained in up to 90% yield by the oxidation of ammonia in special conditions on a catalyst of manganese dioxide or ferric oxide with bismuth oxide as promoter, with medium flow rates and a temperature of  $300^\circ$  (I.G. Farbenind. A.-G., B.P. 325475, 1928; Nagel, *Z. Elektrochem.* 1930, 36, 754; Andrusow, *Angew. Chem.* 1935, 48, 593).

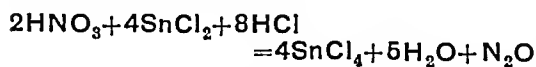
Nitrous oxide is one product of the action of certain metals on nitric acid (*see* p. 539*a*), especially zinc and dilute nitric acid or a mixture of equal volumes of nitric and sulphuric acids diluted with 8-10 vol. of water (Schiff, *Annalen*, 1861, 118, 84):



or the reduction of moist nitric oxide by sulphur dioxide or sulphites:

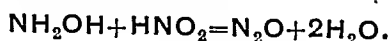


or of nitric acid by stannous chloride:



The last method (Gay-Lussac, *Ann. Chim. Phys.* 1848, [iii], 23, 229) has been proposed (Campari, *Ann. Chim. Farm.* 1888, 8, 253; *Chem. Zentr.* 1888, 1569) as a method of preparation: a mixture of 5 parts of stannous chloride, 10 parts of hydrochloric acid ( $\rho$  1.21), and 0.9 part of nitric acid ( $\rho$  1.38) is heated to boiling. With other proportions explosion may result, and the method is not recommended.

One of the best methods of preparing *pure* nitrous oxide in the laboratory is by mixing solutions of sodium nitrite and hydroxylamine hydrochloride, warming gently if necessary, the gas being passed through ferrous sulphate solution and dried with phosphorus pentoxide (Victor Meyer, *Annalen*, 1875, 175, 141; Partington and Shilling, *Phil. Mag.* 1923, [vi], 45, 416; 1927, [vii], 3, 273):



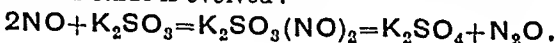
Hyponitrous acid is formed as an intermediate product (p. 533*a*). This gas is free from nitrogen. Nitrous oxide is also formed by the

reduction of nitrous acid with hydrazino (Francke, *Ber.* 1905, 38, 4102).

The usual method of preparation of nitrous oxide, and the one used on the technical scale, is the decomposition of ammonium nitrate by heat:  $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ . Careful attention to detail is necessary. On the small scale, the dry salt is slowly heated in a small retort. It melts, and decomposition begins below  $200^\circ$ , which temperature must not be much exceeded, otherwise the decomposition becomes violent, the gas becomes impure, and a dangerous explosion may result (Veloy, J.C.S. 1883, 43, 370; *Phil. Trans.* 1889, 179, 257). Organic matter must be absent and the ammonium nitrate free from chloride, otherwise carbon dioxide and chlorine, respectively, are formed (Soubeiran, *J. Pharm. Chim.* 1827, 13, 321). The gas is washed with water, ferrous sulphate solution (to remove NO), and sodium hydroxide solution (to remove chlorine and carbon dioxide). It may be collected over warm water. A mixture of 2 parts of ammonium nitrate and 3 parts of dry sand may be heated in a tube at  $260-285^\circ$  (Lidoff, *J. Russ. Phys. Chem. Soc.* 1903, 35, 59; J.C.S. 1903, 84, 361) and the gas washed with a suspension of ferrous sulphate in concentrated sulphuric acid. Heating a mixture of ammonium sulphate (13-14 parts) and sodium nitrate (17 parts) or potassium nitrate (20 parts) at  $240^\circ$  is said to give a regular and quiet evolution of gas (Smith and Elmore, B.P. 9023, 1891; J.S.C.I. 1892, 11, 633, 867; 1893, 12, 10).

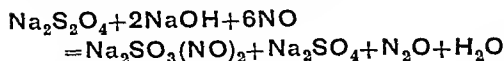
On the large scale not more than 16-18 kg. of ammonium nitrate are heated at a time in a 30-l. cast-iron or aluminium retort; the gas is washed with water, ferrous sulphate solution, and sodium hydroxide solution, then dried and liquefied by compression. The liquid is sold in steel cylinders holding from 6 oz. to 50 lb., and 1 lb. of liquid gives 8.55 cu. ft. of gas at  $15^\circ$ . (Thilo, *Chem.-Ztg.* 1894, 18, 532; Baskerville and Stevenson *J. Ind. Eng. Chem.* 1911, 3, 579 (bibliogr.); H. C. Greenwood, "Industrial Gases," Baillière, 1920, p. 286). The gas taken from such cylinders always contains nitrogen, and a typical analysis quoted by Baskerville and Stevenson (*loc. cit.*; cf. Saunders, J.C.S. 1922, 121, 698) is:  $\text{N}_2\text{O}$  0.6-0.9,  $\text{H}_2\text{O}$  0.15,  $\text{CO}_2$  0-tr.,  $\text{NH}_3$  0.006,  $\text{O}_2$  tr.,  $\text{N}_2$  0.16-3.94%. In the writer's experience the nitrogen content usually exceeds this, except in the gas from a nearly empty cylinder. For anæsthetic purposes the nitrous oxide must be free from chlorine and other oxides of nitrogen, and should contain at least 95% of  $\text{N}_2\text{O}$ . The gas is easily liquefied and was first obtained in liquid form by Faraday (*Phil. Trans.* 1823, 30, 189).

Since nitric oxide is one of the major products of the modern nitrogen industry (p. 557*b*), a possible large-scale method of preparation of nitrous oxide is by a method first described by Davy (*loc. cit.*) and Pelouze (*Ann. Chim. Phys.* 1835, [ii], 60, 161; Luxmoore, J.C.S. 1895, 67, 1019), in which nitric oxide is absorbed in a solution of an alkali sulphite, when a nitrososulphate is formed, and the solution is acidified, when pure nitrous oxide is evolved:





A similar reaction occurs with an alkaline solution of hyposulphite (dithionite):



(Gehlen, Ber. 1931, 64 [B], 1267; 1935, 65 [B], 1130).

**Properties.**—Nitrous oxide is a colourless gas with a faint pleasant sweetish odour and taste, heavier than air ( $\rho$  1.53, air=1). It is respirable and produces anaesthesia, preceded in some cases when the gas is mixed with air or oxygen by pleasurable symptoms and laughter (hence its common name "laughing gas"). It is used as a minor anaesthetic for dental purposes and a special apparatus is used for its administration. Prolonged inhalation causes death.

The molecular structure of nitrous oxide is represented by  $\text{N} \equiv \text{N} = \text{O}$ , corresponding with the electronic formula  $:\text{N}::\text{N}::\text{O}:$ ; the old cyclic formula



and the formula  $\text{N} \rightleftharpoons \text{O} \rightleftharpoons \text{N}$ , are both incorrect (Wierl, Ann. Physik, 1931, 8, 521; Schoemaker and Spurr, J. Amer. Chem. Soc. 1942, 64, 1184; cf. Hunter and Partington, J.C.S. 1933, 309). The normal density is 1.98042  $\pm 0.00005$  g. per l. (Batuecas, J. Chim. phys. 1931, 28, 572) or 1.98034 (Moles, Anal. F's. Quim. 1932, 30, 460). It is more compressible at moderate pressures than an ideal gas, the  $pv$  values decreasing with increase of pressure (Britton, Trans. Faraday Soc. 1929, 25, 520). The coefficient of expansion is 0.003729 (Coppock and Whytlaw-Gray, Proc. Roy. Soc. 1934, 143, 487). The viscosity (Trautz and Kurz, Ann. Physik, 1931, [v], 9, 981) is:

$t^\circ\text{C}.$	26.9	126.9	226.9	276.9
$\eta \times 10^7$	1.488	1.943	2.355	2.555

and Sutherland's constant  $C=286$  (Shilling, Phil. Mag. 1927, [vii], 3, 295). The dielectric constant of the gas at S.T.P. is 1.001129 (Rohman, Ann. Physik, 1911, 34, 979) and at  $100^\circ$  1.0008024 (Czerlinsky, Z. Physik, 1934, 88, 515) and the dipole moment 0.15 D. (Czerlinsky, l.c.). The specific magnetic susceptibility of the gas at  $14^\circ$  is  $\chi = -0.43 \times 10^{-6}$  and those of the liquid and solid are practically the same as this (Soné, Sci. Rep. Tohoku, 1922, 11, 139). The moment of inertia of the molecule is  $66 \times 10^{-40}$  g.-cm.<sup>2</sup> (Plyler and Barker, Physical Rev. 1931, [ii], 38, 1827) and the distance between the nuclei of the end atoms 2.38 Å. (Maxwell, Mosley, and Deming, J. Chem. Physics, 1934, 2, 331; electron diffraction). The refractive index of the gas for  $\lambda=546$   $\mu$ . is 1.000510 (Cuthbertson and Cuthbertson, Phil. Trans. 1914, 213, 23) and for 589  $\mu$ . it is 1.0005122 (Jones and Partington, Phil. Mag. 1915, [vi], 29, 28). The refractive index of the liquid at

$-90^\circ$  is relatively small (Liveing and Dewar, *ibid.* 1892, [v], 34, 205):

$\lambda$ $\mu$ .	670.6	589.6	451.0
$n$	1.3257	1.3305	1.3368

The thermal conductivity of the gas at  $0^\circ$  is  $k=3.64 \times 10^{-5}$  g.-cal. per cm. per sec. per degree (Dickins, Proc. Roy. Soc. 1934, 143, 517) or  $3.8 \times 10^{-5}$  (Ibbs and Hurst, *ibid.* 1929, 123, 134); the temperature coefficient is  $(k_t - k_0)/k_0 t = 0.0047$  (Dickins, l.c.).

The specific heats of the gas are (Shilling, Phil. Mag. 1927, [vii], 3, 297) in g.-cal. per g.-mol.:

$$C_p = 8.659 + 0.00677t - 0.0000022t^2 \\ C_v = 6.629 + 0.00694t - 0.0000241t^2$$

and the ratio of specific heats 1.3046 at  $14.5^\circ$  and 1.2753 at  $100^\circ$  (Partington and Shilling, *ibid.* 1923, [vi], 45, 416; cf. Blue and Giauque, J. Amer. Chem. Soc. 1935, 57, 991; J. R. Partington, "Chemical Thermodynamics," Constable, 1940, p. 207). The entropy per g.-mol. at  $25^\circ\text{C}$ . and 1 atm. is 56.95 units (Blue and Giauque, l.c.) and the 1.14 units discrepancy between the thermodynamic and spectroscopic values is probably due to disordered lattice orientation at very low temperatures.

The critical constants are  $t_c=36.50^\circ$ ,  $p_c=71.65$  atm. (Cardoso and Arni, J. Chim. phys. 1912, 10, 504) and the critical density 0.459 g. per ml. (Quinn and Wernimont, J. Amer. Chem. Soc. 1929, 51, 2002). The density of the liquid at the b.p. is 1.2257 (Grunmach, Ann. Physik, 1904, 15, 401; Sitzungsber. Preuss. Akad. Wiss. Berlin, 1904, 1198). The boiling-point is  $-88.7^\circ$  (Burrell and Robertson, J. Amer. Chem. Soc. 1915, 37, 2691) or  $-88.51^\circ$  (Blue and Giauque, l.c.).

The vapour pressures of the liquid are (Villard, Ann. Chim. Phys. 1897, [vii], 10, 387; Kuenen, Phil. Mag. 1895, [v], 40, 173):

$t^\circ\text{C}.$	0	5	8	12	16	20	25.4	31.5
$p$ atm.	30.75	34.8	37.4	41.2	45.3	49.4	57.45	65.4

Blue and Giauque (l.c.) find  $\log p_{\text{cm}} = -893.56/T + 6.72158$  ( $T$ =absolute temperature). The latent heat of evaporation at the boiling-point is 3,958 g.-cal. per g.-mol., or corrected to ideal gas state of the vapour, 3,972 g.-cal. per g.-mol. (Blue and Giauque, l.c.). Mathias (Ann. Chim. Phys. 1890, [vi], 21, 131) found

$t^\circ\text{C}.$	0	5	10	15	20
$l_e$	58.2	54.6	50.7	46.1	40.8

which are expressed by  $l_e^2 = 131.75(36.4 - t) - 0.928(36.4 - t)^2$ . The surface tension of the liquid at the boiling-point is  $\gamma=26.323$  dynes per cm., which indicates that the liquid is associated (Grunmach, Ann. Physik, 1904, 15, 401; Sitzungsber. Preuss. Akad. Wiss. Berlin, 1904, 1198). The surface tensions between  $-50^\circ$  and  $30^\circ$  are reproduced with an average deviation of 2.6% by van der Waals's equation  $\gamma=72.8(1-T/311.8)^{1.26}$  and the position in the Hildebrand internal pressure series indicates that liquid nitrous oxide should be a slightly better solvent than liquid carbon dioxide (Quinn and Wernimont, J. Amer. Chem. Soc. 1930, 52, 2723). The specific heats of solid

nitrous oxide are (Clusius, Hiller, and Vaughen, *Z. physikal. Chem.* 1930, B, 8, 427):

$T^{\circ}\text{K.}$  . 15.17 22.62 47.22 73.54  
 $C_p$  . . 0.692 1.997 6.165 8.55 g.-cal. per g.-mol.

$T^{\circ}\text{K.}$  . 114.65 178.5 183.7  
 $C_p$  . . 10.57 13.61 18.51 g.-cal. per g.-mol.

\* Liquid; other values for solid, *cf.* Blue and Giauque, *l.c.*

The  $C_p$ -temperature curve is similar to that for carbon dioxide and agrees with a linear molecule.

The densities of the liquid and saturated vapour are (Cailletet and Mathias, *Compt. rend.* 1886, 102, 1202; Villard, *ibid.* 1894, 118, 1096):

$t^{\circ}\text{C.}$	0	5	10	17.5
$\rho$ liq.	0.9105	0.885	0.856	0.804 g. per ml.
$\rho$ vap.	0.087	0.099	0.114	0.146 "

$t^{\circ}\text{C.}$	26.5	32.9	34.9	36.3
$\rho$ liq.	0.720	0.640	0.605	0.572 g. per ml.
$\rho$ vap.	0.207	0.274	0.305	0.338 "

The melting-point of nitrous oxide is  $-90.83^{\circ}$  (Blue and Giauque, *l.c.*). The crystal is cubic (Rehnen, *Physical Rev.* 1912, [ii], 35, 66) and in the lattice the distance  $\text{N}-\text{O}$  is 1.15 Å. The vapour pressure of the solid from  $-90.6^{\circ}$  to  $-144.1^{\circ}$  is given by  $\log p_{\text{mm}} = -1.232.2/T + 9.579$  (Burrell and Robertson, *J. Amer. Chem. Soc.* 1915, 37, 2691) or  $\log p_{\text{mm}} = -1.286/T + 10.13061 - 0.0014038T$  (Blue and Giauque, *l.c.*; *cf.* Black, Van Praagh, and Topley, *Trans. Faraday Soc.*, 1930, 26, 196). The latent heat of sublimation is 5,632 g.-cal. per g.-mol. (Burrell and Robertson, *l.c.*).

The Ostwald ( $\alpha'$ ) and Bunsen ( $\alpha$ ) solubility and absorption coefficients for water are (<sup>1</sup>Geffcken, *Z. physikal. Chem.* 1904, 49, 257; <sup>2</sup>Kuenen, *Physical Rev.* 1922, [iii], 19, 517; <sup>3</sup>Schwab and Berninger, *Z. physikal. Chem.* 1928, 138, 55):

$t^{\circ}\text{C.}$	5	10	15	20	25
$\alpha$ . .	1.048 <sup>1</sup>	0.8778 <sup>1</sup>	0.7377 <sup>1</sup>	0.6204 <sup>1</sup>	0.5443 <sup>1</sup>
$\alpha'$ . .	1.067 <sup>1</sup>	0.9101 <sup>1</sup>	0.7784 <sup>1</sup>	0.6756 <sup>1</sup>	0.5942 <sup>1</sup>

$t^{\circ}\text{C.}$	30	40	50	60	70	80
$\alpha$ . .	—	0.181 <sup>3</sup>	0.150 <sup>3</sup>	0.087 <sup>3</sup>	0.059 <sup>3</sup>	0.055 <sup>3</sup>
$\alpha'$ . .	0.5302	—	—	—	—	—

Henry's law is obeyed at  $25^{\circ}$  (Findlay and Creighton, *J.C.S.* 1910, 97, 549; Findlay and Howell, *ibid.* 1914, 105, 291). The absorption coefficients in alcohol (Carius, *Annalen*, 1855, 94, 129) are:

$t^{\circ}\text{C.}$	0	15	25
$\alpha$ . .	4.178	3.263	2.813

Solubilities in colloidal solutions (Findlay and Howell, *l.c.*), in many salt solutions (Geffcken, *l.c.*; Manchot, Jahrstorfer, and Zepter, *Z. anorg. Chem.* 1924, 141, 45) and organic solvents (Cauquil, *J. Chim. phys.* 1927, 24, 53; Horiuti, *Sci. Pap. Inst. Tôkyô*, 1931, 17, 125; Kunerth, *Physical Rev.* 1922, 19, 512) are available. At low temperatures a crystalline hydrate  $\text{N}_2\text{O} \cdot 6\text{H}_2\text{O}$  is formed (Villard, *Ann. Chim. Phys.* 1897, [vii], 11, 289). The aqueous solution of the gas is neutral, and hyponitrous acid (of which it is formally the anhydride) is not present. There is no satisfactory absorbent for nitrous oxide; absolute alcohol has been used, but the gas is best determined by explosion with hydrogen.

Nitrous oxide is an endothermic compound, the heats of formation being  $Q_p = -20,030$  g.-cal., and  $Q_p = -19,740$  g.-cal., and it is decomposed practically completely when exploded with detonating gas ( $2\text{H}_2 + \text{O}_2$ ). It is much more easily decomposed by heat than nitric oxide; at  $500^{\circ}$  about 1.5% is decomposed and at  $900^{\circ}$  decomposition is practically complete (Berthelot, *Compt. rend.* 1873, 77, 1448). The pure gas rekindles a glowing chip and supports the combustion of carbon, sulphur, phosphorus, and iron wire when these are burning sufficiently vigorously to start the decomposition of the gas. Hunter (*Z. physikal. Chem.* 1905, 53, 441) found the decomposition to be bimolecular:  $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$ , but later experimenters find the reaction in various circumstances to be mainly pseudo-unimolecular and complex (Hinschelwood, *Proc. Roy. Soc.* 1924, 106, 292; Volmer and Kummerow, *Z. physikal. Chem.* 1930, B, 9, 141; Volmer and Bogdan, *ibid.* 1933, B, 21, 257; Melville, *Proc. Roy. Soc.* 1933, 142, 524; *J.C.S.* 1934, 797; Hunter, *Proc. Roy. Soc.* 1934, 144, 386). Appreciable amounts of NO (up to 25% of that required by the equation  $2\text{N}_2\text{O} = 2\text{NO} + \text{N}_2$ ) are formed by the dissociation of  $\text{N}_2\text{O}$  at  $1,300^{\circ}$ . At  $700^{\circ}$  the decomposition is slower and chiefly according to the equation  $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$  (Briner, Meiner, and Rothen, *Helv. Chim. Acta*, 1926, 9, 409; who connect the results with the heats of reaction). Unlike NO, nitrous oxide is not decomposed by compression (Briner and Wroczynski, *Compt. rend.* 1910, 150, 1324). When mixed with oxygen and exposed to ultra-violet light it forms nitrogen and higher oxides (Berthelot and Gaudechon, *ibid.* 1910, 150, 1571; MacDonald, *J.C.S.* 1928, 1). It is readily reduced to nitrogen when mixed with excess of hydrogen and passed through a red-hot tube or over heated platinum or palladium or reduced nickel, no ammonia being formed, and it oxidises a number of heated metals or lower oxides (Sabatier and Senderens, *Compt. rend.* 1902, 135, 278). Potassium and sodium burn to oxides when gently heated in the gas (Gay-Lussac and Thenard, "Recherches physico-chimiques," 1811, 1, 161), but at high temperatures form nitrates. Nitrous oxide is analysed by explosion with hydrogen (Heinzel and Heymann, *Z. Elektrochem.* 1906, 12, 600). Hydrogen burns in nitrous oxide with an enlarged flame and its ignition temperature is lower than in oxygen (Dixon and Higgins, *Manch. Mem.* 1926-27, 71, 15). The velocity of the explosion wave in  $\text{H}_2 + \text{N}_2\text{O}$  in m. per sec. at various initial pressures (Dixon, *Phil. Trans.* 1893, 184, 97) is: 500 mm., 2,094; 760 mm., 2,307; 1,000 mm., 2,302. The velocity is higher in mixtures richer in hydrogen. The velocity of detonation in the  $\text{CO} + \text{N}_2\text{O}$  mixture is 1,106.5 m. per sec. (Berthelot and Vieille, *Ann. Chim. Phys.* 1883, [v], 28, 289). Mixtures of  $\text{N}_2\text{O}$  and carbon disulphide vapour explode with a blue actinic flame, the maximum light emission being for the ratio  $\text{CS}_2:\text{N}_2\text{O} = 1:3.5$  (Van Liempt and de Vriend, *Rec. trav. chim.* 1933, 52, 862). Mixtures of  $\text{N}_2\text{O}$  and  $\text{NH}_3$  are explosive (Dixon, *l.c.*). Nitric Oxide, NO, was the first oxide of nitrogen investigated by Priestley (1772)

("Experiments and Observations on Air," 1774, Vol. I, p. 108; Meldrum, J.C.S. 1933, 902). It is formed by direct union of oxygen and nitrogen by several methods. It is produced, together with ozone (the production of which it inhibits), by the action of the silent electric discharge (Manchot, Ber. 1908, 41, 471), when air is passed slowly over a glowing Nernst filament (Fischer and Marx, *ibid.* 1906, 39, 3631), in the electric arc and spark discharges in air, in various flames (of hydrogen, carbon monoxide, ethylene, etc.), and at white-hot solid surfaces (Haber and Coates, Z. physikal. Chem. 1909, 69, 337). Nitric oxide results from a cold direct-current discharge from an oxide cathode in a mixture of nitrogen and oxygen at 6 mm. pressure, the velocity of formation being constant for nitrogen contents from 20 to 80% and zero outside these limits (Schwab and Loeb, *ibid.* 1924, 114, 23).

In the combustion of hydrogen in air at ordinary pressures practically no nitric oxide is formed, but at 20 atm. pressure 0.3 mol. of NO is formed for 100 mol. of water. With an equimolecular mixture of nitrogen and oxygen the yield is still small at low pressures but is at least 3 mol. of NO per 100 mol. of water at 15 atm. pressure, there being little increase in the yield up to 50 atm. pressure (Wolokitin, Z. Elektrochem. 1910, 16, 814). Nitric oxide is formed in appreciable amount in the combustion of hydrogen in oxygen containing a little nitrogen (Kolbe, Annalen, 1861, 119, 176).

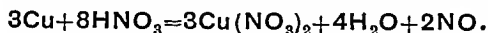
A high temperature favours a rapid rate of formation and a high yield of nitric oxide from nitrogen and oxygen, but also favours its dissociation, so that rapid cooling is necessary (Nernst, Z. anorg. Chem. 1906, 49, 212; Haber, *et al.*, Z. Elek'rochem. 1910, 16, 810; Fischer and Hene, Ber. 1912, 45, 3652; v. 1913, 46, 603; Koenig, *ibid.* 1913, 46, 132; v. NITROGEN, ATMOSPHERIC, UTILISATION OF, p. 544a).

Nitric oxide is formed in small amount by sparking a mixture of nitrogen and steam, or passing it through an iridium tube at 2,000° (Tower, *ibid.* 1905, 38, 2945):



Nitric oxide is produced by the action of a variety of reducing agents on higher oxides of nitrogen, and on nitrous and nitric acids:

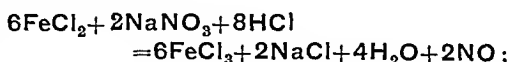
1. The action of nitric acid of  $\rho$  1.2 (equal volumes of concentrated acid and water) in the cold on copper, conveniently in the form of turnings (Millon, Ann. Chim. Phys. 1842, [iii], 6, 73, 95; 1843, [iii], 7, 320; Stansbie, J.S.C.I. 1913, 32, 311):



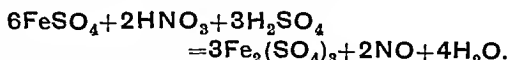
The successive addition of small amounts of concentrated nitric acid to copper turnings covered with water has also been recommended. The gas so prepared, especially in the later stages of the reaction, contains nitrous oxide (Carius, Annalen, 1855, 94, 138). It may be purified by dissolving in cold ferrous sulphate solution and expelling again by warming (Carius, *l.c.*; Oppenheimer, Ber. 1903, 36, 1744). Kaemmerer (*ibid.* 1885, 18, 3064) dropped concentrated sulphuric acid on copper foil in

saturated sodium nitrate solution. Rennie, Higgin, and Cooke (J.C.S. 1908, 93, 1162) find that  $\text{Cu}(\text{NO}_3)_2$  strongly accelerates the reaction between Cu and  $\text{HNO}_3$ ;  $\text{NaNO}_3$  accelerates it, and  $\text{RbNO}_3$  and  $\text{CsNO}_3$  may either accelerate or retard it (*ibid.* 1911, 99, 1035).

2. Heating a solution of an alkali nitrate and ferrous chloride in hydrochloric acid (Pelouze, quoted by Gay-Lussac, Ann. Chim. Phys. 1848, [iii], 23, 216):

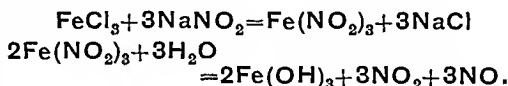


or heating a solution of nitric acid or an alkali nitrate, ferrous sulphate, and dilute sulphuric acid:



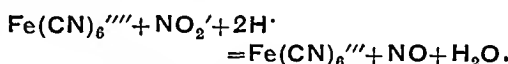
This product is much purer than that obtained by process (1).

3. The action of ferric chloride solution on sodium nitrite:

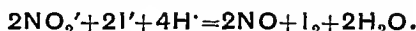


If the sodium nitrite is placed under carbon disulphide and a suspension of ferric chloride in carbon disulphide added, the  $\text{NO}_2$  remains in solution and nitric oxide is evolved (Matuschek, Chem.-Ztg. 1905, 29, 31).

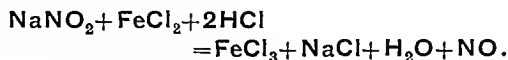
4. Dropping a solution of sodium nitrite and potassium ferrocyanide into dilute acetic acid gives a very pure gas (Deventer, Ber. 1893, 26, 589):



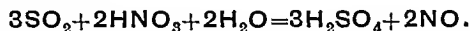
5. Dropping 50% sulphuric acid into a concentrated solution of equimolecular amounts of potassium iodide and sodium nitrite gives very pure nitric oxide (Winkler, *ibid.* 1901, 34, 1412; Johnston and Giauque, J. Amer. Chem. Soc. 1929, 51, 3194):



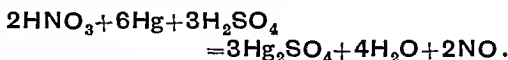
6. The action of ferrous chloride and hydrochloric acid on sodium nitrite (Thiele, Annalen, 1889, 253, 246):



7. Passing sulphur dioxide into warm nitric acid of  $\rho$  1.15 (Weber, Ann. Phys. Chem. 1867, 130, 277):

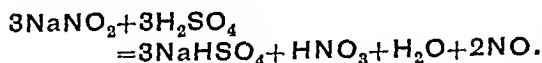


8. Agitating mercury with a solution of nitric acid or a nitrate in concentrated sulphuric acid (Crum, Annalen, 1847, 62, 233; Emich, Monatsh. 1892, 13, 73):



This reaction occurs in Lunge's nitrometer (Ber 1878, 11, 434).

9. Dropping concentrated sulphuric acid on sodium nitrite covered with water (Noyes, J. Amer. Chem. Soc. 1925, 47, 2170):



10. Electrolysis of a mixture of nitric and nitrous acids (Meister, Lucius, and Brüning, G.P. 244362, 1912) at the ordinary temperature.

The gas is purified by absorption in cold ferrous sulphate solution and expelling it again by gentle heating, when the first portion (only) of the gas is pure (*see* Carius, under (1) above), so that this process should not be used with pure gas prepared by method (4), (5), or (8).

Moser (Z. anal. Chem. 1911, 50, 401) considers that methods (5) and (8) are the best, but (4) is very convenient and gives a pure gas (Partington and Shilling, Phil. Mag., 1923, [vi], 45, 416).

*Properties.*—Nitric oxide is a colourless gas, sparingly soluble in water and (unlike nitrous oxide) liquefied only with difficulty. Its structure is uncertain, since the molecule contains an odd electron (as is shown by the paramagnetism of the gas), but it is probably best represented as a resonance hybrid between the forms  $\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}\text{:}$  and  $\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}\text{:}$  which may be symbolised as a molecule with a three-electron bond (Pauling, J. Amer. Chem. Soc. 1931, 53, 3225)  $\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}\text{:}$ , which stabilises the molecule so that it does not associate to  $\text{N}_2\text{O}_2$ , except perhaps in the liquid state or when adsorbed on surfaces. This formula is in agreement with the small dipole moment of the gas, which indicates that the molecule has a high degree of symmetry.

The normal density is 1.3402 g. per l. (Gray, J.C.S. 1905, 87, 1601; Guye and Davila, Compt. rend. 1905, 141, 826). The gas shows only a small divergence from Boyle's law at lower pressures (Jaquerod and Schener, *ibid.* 1905, 140, 1384). The coefficient of expansion (mean between  $-135^\circ$  and  $0^\circ$ ) is 0.0037074 (Adwentowski, Bull. Acad. Sci. Cracow, 1909, 742). The viscosity is (Trautz and Gabriel, Ann. Physik, 1931, 11, 606):

$t^\circ\text{C.}$	20	50	100	150	200	250
$\eta \times 10^7$	1.882	2.032	2.272	2.492	2.704	2.885

and the Sutherland constant  $C=167$  (Vogel, *ibid.* 1914, 43, 1235). The dielectric constant is 1.00593 at  $25^\circ$  and the dipole moment 0.16 D. (Watson, Rao, and Ramaswamy, Proc. Roy. Soc. 1933-34, 143, 558). The gas is paramagnetic, the specific magnetic susceptibility being  $\chi=48.8 \times 10^{-6}$  at  $20^\circ$  (Soné, Sci. Rep. Tôhoku, 1922, 11, 139). The moment of inertia is not accurately known, the values given varying between  $2.2 \times 10^{-40}$  and  $24.8 \times 10^{-40}$  g.-cm.<sup>2</sup>; Snow, Rawlins, and Rideal (Proc. Roy. Soc. 1929, 124, 453) found  $16.4 \times 10^{-40}$  g.-cm.<sup>2</sup>.

The refractive index of the gas is 1.000297 for sodium light (Mascart, Compt. rend. 1874, 78, 617), 1.0002939 for  $\lambda=589$  m $\mu$ . (Cuthbertson and Metcalfe, Proc. Roy. Soc. 1908, 80, 406; *cf.* Jones and Partington, Phil. Mag. 1915, 29, 28). The thermal conductivity at  $55^\circ$  is  $k=546 \times 10^{-7}$  g.-cal. per cm. per sec. per degree (Todd, Proc. Roy. Soc. 1910, 83, 19).

The specific heat of the gas is  $C_p=7.26$  at  $-55^\circ$  and  $7.25$  at  $15^\circ$  (in g.-cal. per g.-mol.) (Heuse, Ann. Physik, 1919, 59, 86) and the ratio of specific heats  $c_p/c_v=1.400$  at  $7.0^\circ$ , giving  $C_v=4.99$  and  $C_p=6.99$  g.-cal. per g.-mol. (Partington and Shilling, Phil. Mag. 1923, [vi], 45, 416; theoretical values in Johnston and Chapman, J. Amer. Chem. Soc. 1933, 55, 153; and Witmer, *ibid.* 1934, 56, 2229). The entropy and free energy are calculated by Witmer (*l.c.*; *cf.* Johnston and Chapman, *l.c.*).

The critical constants are  $t_c=-93.5^\circ$  and  $p_c=71.2$  atm. and the critical density 0.520 g. per ml. (Olszewski, Compt. rend. 1885, 100, 940). The density of the liquid at the boiling-point is unusually high, 1.269 (Adwentowski, Bull. Acad. Sci. Cracow, 1909, 742; *cf.* Cheesman, below) and, with the vapour-pressure curve, is thought to indicate association to  $\text{N}_2\text{O}_2$ . The boiling-point is  $-153.6^\circ$  (Olszewski, *l.c.*) or  $121.36^\circ$  K. (Johnston and Giauque, J. Amer. Chem. Soc. 1929, 51, 3194; no value for the absolute temperature of  $0^\circ\text{C.}$  is given); the liquid is blue. The vapour pressures of the liquid are given by  $\log p_{\text{cm.}}=-776/T-0.002364T+8.562128$  (Johnston and Giauque, *l.c.*). The latent heat of evaporation at the boiling-point is 3,292.6 g.-cal. per g.-mol. (Johnston and Giauque, *l.c.*) and the surface tensions,  $\gamma$ , and densities of the liquid (Cheesman, J.C.S. 1932, 889):

$t^\circ\text{C.}$	-163	-156	-153.6
$\gamma$ dynes per cm.	27.79	24.12	22.11
Density, g. per ml.	1.332	1.277	1.227

The melting-point is  $-167.0^\circ$  (Olszewski, *l.c.*) or the triple point  $109.49^\circ$  K. (Johnston and Giauque, *l.c.*); the solid is blue. The vapour pressure of the solid at the melting-point is 138 mm. (Olszewski, *l.c.*) or is given by the equation  $\log p_{\text{cm.}}=-867/T+0.00076T+9.05125$  (Johnston and Giauque, *l.c.*). The density of the solid at  $20.4^\circ$  K. is 1.57 (Heuse, Z. physikal. Chem. 1930, 147, 226) and at  $0^\circ$  K. is calculated as 1.58 (London, *ibid.* 1930, B, 11, 222). The latent heat of sublimation is 3,863 g.-cal. per g.-mol. (Goldschmidt, Z. Physik, 1923, 20, 159). The specific heats of the liquid and solid have been determined down to  $15.5^\circ$  K. (Johnston and Giauque, *l.c.*).

The heat of formation of NO (which is endothermic) at room temperature is  $-21,575$  g.-cal. (J. Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882, Vol. II, p. 198) or  $-21,600$  g.-cal. per g.-mol. (Berthelot, Compt. rend. 1880, 90, 782).

The Bunsen absorption coefficient,  $a$ , in water (Winkler, Ber. 1901, 34, 1408; Z. physikal. Chem. 1892, 9, 171) is:

$^\circ\text{C.}$	$a$	$^\circ\text{C.}$	$a$
0	0.07381	40	0.03507
5	0.06461	50	0.03152
10	0.05709	60	0.02854
15	0.05147	70	0.02610
20	0.04706	80	0.02700
25	0.04323	90	0.02648
30	0.04001	100	0.02623

The gas is more soluble (0.316 at  $0^\circ$ , 0.286 at  $10^\circ$ , 0.2659 at  $20^\circ$ ) in alcohol than in water (Carius, Annalen, 1885, 94, 138). It is only sparingly soluble in concentrated sulphuric acid

(Lunge, Ber. 1885, 18, 1391; Tower, Z. anorg. Chem. 1906, 50, 382).

Nitric oxide is the most stable oxide of nitrogen. At 700° only 0.5% is dissociated into nitrogen and oxygen, and at 1,000° only 3-4%. The kinetics of the change  $2\text{NO}=\text{N}_2+\text{O}_2$  (Muthmann and Hofer, Ber. 1903, 36, 438; Nernst, Z. anorg. Chem. 1906, 49, 213; Jellinek, *ibid.* 1906, 49, 229; Brode, Z. Elektrochem. 1905, 11, 752; Briner and Boubnoff, Compt. rend. 1913, 156, 228; v. NITROGEN, ATMOSPHERIC, UTILISATION OF, p. 558*d*) have been studied at various pressures (up to 700 atm.) and temperatures ( $-90^\circ$  upwards). A secondary reaction is  $4\text{NO}=2\text{N}_2\text{O}+\text{O}_2$ , and  $\text{NO}_2$  is formed at lower temperatures by the action of the oxygen formed in the decomposition on the unchanged  $\text{NO}$  (Guye and Schneider, Helv. Chim. Acta, 1918, 1, 33).

At ordinary temperature nitric oxide combines with oxygen to form a red gas, nitrogen peroxide,  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , by a termolecular reaction:  $2\text{NO}+\text{O}_2=2\text{NO}_2$ ; according to Emich (Monatsh. 1892, 13, 86), Chapman (J.C.S. 1937, 1991), and Stoddart (*ibid.* 1939, 5) even if the gases are dried with phosphorus pentoxide, whilst Baker (J.C.S. 1894, 65, 611; 1929, 1661) states that the very dry gases do not react. According to Raschig (Z. angew. Chem. 1904, 17, 1398, 1777) and Sanfourche (Compt. rend. 1919, 168, 307, 401) the first very rapid stage of the reaction, independent of temperature between  $-50^\circ$  and  $525^\circ$ , is  $4\text{NO}+\text{O}_2=2\text{N}_2\text{O}_3$ , which is followed by a slower reversible reaction:  $2\text{N}_2\text{O}_3+\text{O}_2\rightleftharpoons 4\text{NO}_2$ . Raschig (Raschig and Prah, Z. angew. Chem. 1929, 42, 253) afterwards abandoned this hypothesis (which still appears in the technical literature) and it is now generally recognised that the oxidation proceeds directly to  $\text{NO}_2$  by a termolecular reaction, the first half of the reaction being much faster than the second, which produces an illusion of an oxidation in stages (Bodenstein, Z. Elektrochem. 1918, 24, 183; Z. angew. Chem. 1918, 31, i, 145; cf. Todd, Phil. Mag. 1918, 35, 281, 435; Briner and Fridöri, Helv. Chim. Acta, 1918, 1, 181; Trautz, Z. Elektrochem. 1919, 25, 4; Wourzel, Compt. rend. 1920, 170, 109, 229; Briner and Malet, J. Chim. phys. 1923, 20, 173; Briner, Pfeiffer, and Malet, *ibid.* 1924, 21, 25, 45, with bibliography; Hasche, J. Amer. Chem. Soc. 1926, 48, 2253; Kornfeld and Klingler, Z. physikal. Chem. 1929, 4B, 37; Berthoud, J. Chim. phys. 1933, 30, 337; Smith, J. Amer. Chem. Soc. 1943, 65, 74). According to Wourzel (*l.c.*) the velocity of oxidation is given by

$$-dp_{\text{NO}}/dt = kp_{\text{NO}}^2p_{\text{O}_2}$$

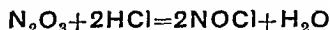
where  $t$  is in seconds and  $p$  is in mm. Hg, and the velocity coefficient at different temperatures is:

$t^\circ\text{C.}$	0	25.2	85.5	100	150
$10^\circ\text{K.}$	10.63	8.73	5.69	4.8	3.35

The negative temperature coefficient of  $k$  has been explained by supposing that nitric oxide reacts in the form  $(\text{NO})_2$ , the equilibrium  $(\text{NO})_2\rightleftharpoons 2\text{NO}$  being displaced to the right with rise of temperature. The oxidation re-

action is catalysed by silica gel (Hasche and Patrick, J. Amer. Chem. Soc. 1925, 47, 1207; Saposhnikov, Okatov, and Susarov, J. Russ. Phys. Chem. Soc. 1929, 61, 1353; Szegeő and Guacci, Gazzetta, 1931, 61, 333; Verhoek and Daniels, J. Amer. Chem. Soc. 1931, 53, 1250, for the reaction  $\text{NO}+\text{NO}_2=\text{N}_2\text{O}_3$ ).

Under high pressure in sealed tubes  $\text{NO}$  gas and liquid decompose, the change being first apparent at about 28 atm. and rapid at 700 atm., and drops of blue liquid  $\text{N}_2\text{O}_3$  separate:  $6\text{NO}=2\text{N}_2\text{O}_3+\text{N}_2$ . If hydrogen chloride is present nitrosyl chloride is formed:



(Briner and Wroczyński, Compt. rend. 1909, 149, 1372; Briner, Biedermann, and Rothen, Helv. Chim. Acta, 1925, 8, 923; Briner, *ibid.* 1942, 25, 1515).

The same change occurs in presence of water or alkali (when nitrite is formed from the  $\text{N}_2\text{O}_3$ ), so that the gas cannot be kept in a pure state over water (Gay-Lussac, Ann. Chim. Phys. 1816, [ii], 1, 394; Russell and Lapraik, J.C.S. 1877, 32, 35; Cooke, Chem. News, 1888, 58, 103, 155) although the dry or moist gas can be kept over mercury for any length of time (Emich, Monatsh. 1892, 13, 90; Zimmermann, *ibid.* 1905, 26, 1277; Moser, Z. anal. Chem. 1911, 50, 401; Barnes, J.S.C.I. 1926, 45, 259*r*; J.C.S. 1931, 2605). Nitric oxide is decomposed by finely divided nickel suspended in hot water with the production of nitrogen and nickel oxide (Felgate, Chem. News, 1913, 108, 178), and some metals reduced in hydrogen are readily oxidised at a comparatively low temperature with formation of nitrogen.

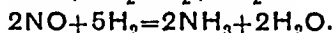
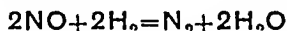
According to Schönbein (whose statements are frequently inaccurate) nitric oxide is oxidised to nitrous and nitric acids by hydrogen peroxide, to nitrite by suspensions of  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{MnO}_2$ , and  $\text{Ag}_2\text{O}$  in water, to nitrate by potassium permanganate, and to nitric acid by iodine. Chlorine dioxide gives  $\text{NO}_2$ , and hypochlorous acid forms nitric acid (Balard). In the dry state nitric oxide acts on many oxidising agents, forming nitrite and nitrate (Auden and Fowler, Chem. News, 1895, 72, 163). When nitric oxide is bubbled through liquid oxygen, or when air acts on solid  $\text{NO}$  at  $-185^\circ$ , or when an electric discharge is passed through liquid air, a green solid is formed which has been variously described as  $\text{N}_2\text{O}_3$  (Helbig, Atti R. Accad. Lincei, 1903, 12, 166),  $\text{NO}_3$  (F. Raschig, Chem.-Ztg. 1911, 35, 1096; "Schwefel- und Stickstoffstudien," Verlag Chemie, 1924, p. 20), and  $\text{N}_3\text{O}_4$  (Hasche, J. Amer. Chem. Soc. 1925, 47, 2143). At a slightly higher temperature it forms blue  $\text{N}_2\text{O}_3$ .

Nitric oxide and hydrogen chloride at  $-180^\circ$  form a solid having an intense purple colour and melting at about  $-150^\circ$  to a purple liquid. The vapour pressure is near that of nitric oxide so that the complex is very unstable and is probably, in view of its colour, of the type  $[\text{NOH}]^+\text{Cl}^-$  (Rodebush and Yntema, *ibid.* 1923, 45, 332).

Nitric oxide and sulphur trioxide react at  $60^\circ$  to form a substance identical with that formed from  $\text{NO}_2$  and sulphur dioxide at  $200^\circ$ . This

was thought to be  $2\text{SO}_3\cdot\text{NO}$  (Manchot, König, and Reimlinger, Ber. 1926, 59 [B], 2672), but it is identical with the nitrosylsulphuric anhydride,  $\text{O}(\text{NO}\cdot\text{O}\cdot\text{SO}_2)_2$ , or nitrosyl disulphate,  $(\text{NO})_2\text{S}_2\text{O}_7$ , correctly analysed by de la Provostaye in 1840 (Ann. Chim. Phys. 1840, [ii], 73, 362; Pictet and Karl, Bull. Soc. chim. 1908, [iv], 3, 1114; Briner, Lunge, and Van der Wijk, Helv. Chim. Acta, 1928, 11, 1125; Manchot, Ber. 1929, 62 [B], 1261).

Nitric oxide may be reduced in a variety of ways, giving nitrogen, ammonia, and (with hydrogen sulphide, alkali sulphides, sulphurous acid, and phosphine) nitrous oxide. Alkaline pyrogallol reduces it fairly rapidly to nitrous oxide, but about 20% is absorbed (Oppenheimer, *ibid.* 1903, 36, 1744). Hydriodic acid forms ammonia, stannous chloride gives hydroxylamine and ammonia, and in alkaline solution also some hyponitrite. Chromous salts in neutral solution give deep-red solutions containing ammonia; in acid solutions hydroxylamine is formed, sometimes quantitatively (Chesneau, Compt. rend. 1899, 129, 100; Kohl-schütter, Ber. 1904, 38, 3053). A mixture of nitric oxide and hydrogen when passed over heated platinum sponge is violently reduced to ammonia (Kuhlmann, Annalen, 1839, 29, 272), and when passed over heated nickel, ammonia and some nitrogen are formed (Sabatier and Senderens, Compt. rend. 1902, 135, 278; Neogi and Adhicary, Z. anorg. Chem. 1910, 69, 209; Guye and Schneider, Helv. Chim. Acta, 1918, 1, 33):



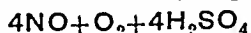
Reaction begins at  $300^\circ$  and is then very rapid, but it still proceeds at  $120^\circ$  when once begun. No  $\text{N}_2\text{O}$  is formed. At  $250\text{--}300^\circ$ , 70% of the NO is converted into ammonia. When the gas mixture  $\text{NO} + 3\text{H}_2$  is passed over heated finely divided tin, reduced iron or zinc dust, an almost quantitative yield of ammonia is obtained (Adhicary, Chem. News, 1915, 112, 163). In the cold and in presence of water and platinum black, some ammonia and hydroxylamine are slowly formed from a mixture of nitric oxide and hydrogen (Butterworth and Partington, Trans. Faraday Soc. 1930, 26, 144).

Fluorine gives  $\text{NO}_2\text{F}$  (*q.v.*); chlorine and bromine form the halides  $\text{NOCl}$  and  $\text{NOBr}$  (see "Halides of Nitrous Acid," p. 531a), but iodine does not react.

Since nitric oxide is a stable gas—it does not decompose appreciably below  $1,000^\circ$ —it does not support combustion readily and extinguishes a burning taper, burning sulphur, and feebly burning phosphorus. E. Mitscherlich ("Lehrbuch der Chemie," Mittler, Berlin, 1831, Vol. I, p. 347) and Berthelot (Ann. Chim. Phys. 1869, [iv], 18, 76) say glowing charcoal burns in the gas. Brightly burning phosphorus burns brilliantly, a little  $\text{NO}_2$  being formed. Heated potassium, but not sodium, burns in the gas, liberating nitrogen (Gay-Lussac and Thenard, "Recherches physico-chimiques," 1811, 1, 161). A mixture of nitric oxide and carbon disulphide vapour burns with a brilliant blue flame (Berzelius, "Lehrbuch der Chemie,"

Dresden, 1825, Vol. I, Pt. ii, p. 485); in a long tube a detonation wave is set up (Dixon, Phil. Trans. 1903, 200, 315). Nitric oxide has an influence on the reactions in a methane-oxygen flame (Reis and Waldbauer, Z. physikal. Chem. 1913, 85, 62), and in small amounts it reacts in many cases with free radicals and breaks reaction chains in which they play a part (Staveley and Hinshelwood, Proc. Roy. Soc. 1936, A, 154, 335; J.C.S. 1936, 812, 818).

Nitric oxide and oxygen (or air) react rapidly in presence of concentrated sulphuric acid to form nitrososulphuric acid  $\text{SO}_2(\text{OH})\cdot\text{O}\cdot\text{NO}$ , and no nitric acid is formed even if the oxygen is in excess (Lunge, Ber. 1885, 18, 1384):



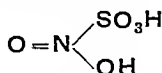
When rapidly mixed with air or oxygen over alkali solution almost pure nitrite is formed (Gay-Lussac, Ann. Chim. Phys. 1816, [ii], 1, 394):  $4\text{NO} + \text{O}_2 + 4\text{NaOH} = 4\text{NaNO}_2 + 2\text{H}_2\text{O}$ .

Nitric oxide reduces nitric acid above a certain concentration to  $\text{N}_2\text{O}_3$  or  $\text{NO}_2$  (Saposhnikov, J. Russ. Phys. Chem. Soc. 1901, 33, 506), and it is absorbed by phosphoric acid (Reinsch, J. pr. Chem. 1843, [i], 28, 385), arsenic acid, and some organic acids, and by many halides, such as those of boron, silicon, copper, bismuth, and iron, forming, for example,  $2\text{FeCl}_2\cdot\text{NO}$  (Besson, Compt. rend. 1889, 108, 1012; Thomas, Ann. Chim. Phys. 1898, [vii], 13, 145).

Nitric oxide, as Priestley found, is absorbed by cold ferrous sulphate solution to form a black liquid, which apparently contains an unstable compound  $[\text{Fe}(\text{NO})]\text{SO}_4$  with the complex cation  $\text{Fe}(\text{NO})^{++}$  (Manchot and Zeehtenmayer, Annalen, 1906, 350, 365; Hüfner, Z. physikal. Chem. 1907, 59, 416; Usher, *ibid.* 1908, 62, 622; Zimmermann, Monatsh. 1905, 26, 1277), and  $[\text{Fe}(\text{NO})]\text{HPO}_4$  separates in blackish-brown crystals on adding alcohol to a ferrous salt solution containing ammonium phosphate which is saturated with nitric oxide (Manchot and Huttner, Annalen, 1910, 372, 153; Manchot, Ber. 1914, 47, 1601, 1614; Bellucci, Gazzetta, 1914, 44, ii, 384). Nitric oxide is also absorbed by solutions of copper, manganese, and nickel salts (Hüfner, *l.c.*; Usher, *l.c.*). A compound of ferrous selenate and nitric oxide,  $[\text{Fe}(\text{NO})]\text{SeO}_4\cdot 4\text{H}_2\text{O}$ , separates in brownish-black unstable crystals, which lose NO in air, on passing nitric oxide to saturation into a concentrated solution of ferrous selenate containing a little selenic acid, cooling and adding a large excess of absolute alcohol saturated with nitric oxide (Manchot and Linekh, Z. anorg. Chem. 1924, 140, 37). Nitric oxide is absorbed by a solution of ferric sulphate in 90% sulphuric acid to form a deep red liquid apparently containing  $\text{Fe}_2(\text{SO}_4)_3\cdot\text{NO}$ , which can be obtained in crystals mixed with ferric sulphate (Manchot, Annalen, 1910, 372, 179), and the violet solution formed by passing the gas into a solution of copper sulphate in concentrated sulphuric acid probably contains an unstable compound  $\text{CuSO}_4\cdot\text{NO}$  (Manchot, *ibid.* 1911, 375, 308). These coloured compounds were regarded by Raschig (Z. angew. Chem. 1904, 17, 1398,

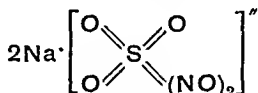


1777; 1905, 18, 1281, 1308; 1907, 20, 694; Ber. 1907, 40, 4582; J.S.C.I. 1911, 30, 166) as salts of an acid  $\text{H}_2\text{SNO}_5$  or



(e.g.,  $\text{FeSNO}_5$ , which is the same empirical formula as Manchot's  $[\text{Fe}(\text{NO})]\text{SO}_4$ ) and by Sabatier (Compt. rend. 1896, 122, 1417, 1479, 1537; 123, 255; cf. Lunge and Berl, Z. angew. Chem. 1906, 19, 807, 857, 881) as salts of an acid  $\text{NO}(\text{SO}_3\text{H})_2$ , but Manchot's formulation, e.g.,  $[\text{Fe}(\text{NO})]\text{SO}_4$ , as nitroso-compounds, is usually preferred. The black colour formed with ferrous sulphate solution is the basis of the so-called "brown-ring test" for nitrates, described by Desbassins de Richemont in 1835 and by Wackenroder (Annalen, 1836, 18, 152, 157), both of whom mention that the colour is bright-red in concentrated sulphuric acid.

Nitric oxide is slowly absorbed by potassium permanganate or dichromate solution (Ellingham, J.C.S. 1932, 1565), but the best absorbent is a slightly alkaline solution of sodium sulphite, when a compound  $\text{Na}_2\text{SO}_3(\text{NO})_2$  is formed. This probably has the structure



(Weitz and Achterberg, Ber. 1936, 66 [B], 1718, 1728).

The complex *Roussin's salts* (v. Vol. VII, 60c) and the *nitroprussides* (v. Vol. III, 477a) are also nitroso-compounds, and complex metallic amines containing NO are also known.

**Dinitrogen Trioxide or Nitrous Anhydride,  $\text{N}_2\text{O}_3$ .**—The formation of red fumes by the reduction of nitric acid by heat and by the action of metals was well known to the alchemists. Priestley observed their formation from nitric oxide and air. He called the product "nitrous vapour" and made a large number of excellent experiments with it, so that his "Experiments and Observations on Air," especially the revised edition (3 vol., 1790) may still be consulted with advantage (cf. Meldrum, J.C.S. 1933, 902). The existence of the oxides  $\text{N}_2\text{O}_3$  ("acide pernitreux") and  $\text{NO}_2$  ("acide nitreux") was first recognised by Gay-Lussac (Ann. Chim. Phys. 1816, [ii], 1, 394) and by Dulong (*ibid.* 1816, [iii], 2, 317) who showed that the final product of the combination of NO and oxygen, and of the action of heat on lead nitrate, is not  $\text{N}_2\text{O}_3$  ("acide nitreux" of Dulong) but  $\text{NO}_2$  ("acide hypazotique" of Dulong). F. Raschig ("Schwefel- und Stickstoffstudien," Verlag Chemie, 1924, p. 20) for long supposed that  $\text{N}_2\text{O}_3$ ,  $\text{NO}_3$ , and  $\text{N}_2\text{O}_4$  are the initial products of the action of oxygen on nitric oxide, but he later abandoned these erroneous views (Raschig and Prahl, Z. angew. Chem. 1929, 42, 611). The researches of Bodenstein (Z. Elektrochem. 1918, 24, 183; Z. angew. Chem. 1918, 31, 145; Z. physikal. Chem. 1922, 100, 68; 1936, 175, 294) show quite clearly that the only product of the reaction at ordinary temperatures is  $\text{NO}_2$ . The green substance

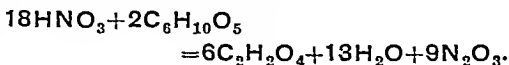
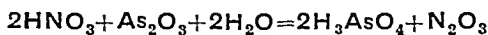
supposed by Raschig to be  $\text{NO}_3$  can be exactly imitated in colour by dipping a test-tube containing liquid air into liquid nitrogen trioxide and then into liquid nitrogen tetroxide, when superposed layers of blue and yellow are formed (Müller, Z. anorg. Chem. 1912, 76, 324; 1914, 86, 230).

When NO and gaseous  $\text{NO}_2$  are mixed there is no change in volume (Ramsay and Cundall, J.C.S. 1885, 47, 187, 672; 1890, 57, 590; Chem. News, 1894, 70, 187; Lunge and Porschnew, Z. anorg. Chem. 1894, 7, 209), hence it was argued that no combination occurred, and that  $\text{N}_2\text{O}_3$  is completely dissociated in the gaseous state. Dixon and Peterkin (J.C.S. 1899, 75, 613; Wourtsel, Compt. rend. 1920, 170, 109; Purcell and Cheesman, J.C.S. 1932, 826) showed, however, that if due allowance is made for the displacement of the equilibrium  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  to the right when the volume is increased by mixing with NO, according to Gibbs's formula (p. 525c), the results indicate that at 27° the gas contains about 3% by volume of  $\text{N}_2\text{O}_3$  in equilibrium with  $\text{N}_2\text{O}_4$ ,  $\text{NO}_2$ , and NO.

When the red gas is cooled below 0° it condenses to a deep blue liquid which probably consists mainly of  $\text{N}_2\text{O}_3$  molecules, but on evaporation this again dissociates almost completely into NO,  $\text{NO}_2$ , and  $\text{N}_2\text{O}_4$ . When the blue liquid is dried by prolonged exposure to phosphorus pentoxide it becomes green (Gaines, Chem. News, 1883, 48, 97) and the vapour density ( $H=1$ ) of the gas formed from this very dry liquid was 38.1–62.2 ( $\text{N}_2\text{O}_3=38$ ) according to the period of drying (4–33 days), but the density did not increase regularly with the period of drying, the results for 4 and for 22 days, for example, being the same. The molecular weights in solution in benzene (on which  $\text{N}_2\text{O}_3$  is without action) were, however, found to be 83–95 ( $\text{N}_2\text{O}_3=76$ ). The conclusion drawn from these experiments is that very dry nitrogen trioxide can exist in the gaseous state as  $\text{N}_4\text{O}_6$  (cf.  $\text{P}_4\text{O}_6$ ,  $\text{As}_4\text{O}_6$ ), but in presence of a trace of moisture this breaks up almost completely into NO,  $\text{NO}_2$ , and  $\text{N}_2\text{O}_4$  (H. B. and M. Baker, J.C.S. 1900, 77, 647; 1907, 91, 1862; B. M. Jones, *ibid.* 1914, 105, 2301). Other experimenters (D. L. and M. Chapman, *ibid.* 1937, 1991) failed to confirm the higher vapour densities of dry nitrogen trioxide. Stoddart (J.C.S. 1945, 448) found that phosphorus pentoxide forms a compound  $\text{P}_2\text{O}_5(\text{NO})_2$  in contact with liquid  $\text{N}_2\text{O}_3$ , and as the latter then contains an excess of  $\text{N}_2\text{O}_4$  its green colour, and the higher vapour density, are due to the presence of this  $\text{N}_2\text{O}_4$ .

In what follows the gaseous product of the preparations must be understood to be mainly a mixture of nitric oxide and nitrogen peroxide, containing perhaps 1 or 2% of  $\text{N}_2\text{O}_3$ , but the blue liquid produced is probably mainly  $\text{N}_2\text{O}_3$ .

**Preparation.**—1. By the reduction of nitric acid of suitable concentration by heating with arsenious oxide or starch:





Acid of  $\rho$  1.20 gives NO, acid of  $\rho$  1.35 gives  $\text{N}_2\text{O}_3$ , and acid of  $\rho$  1.50 gives practically only  $\text{NO}_2$  (Lunge, Ber. 1878, 11, 1229, 1641; 1885, 18, 1376; Lunge and Porschnow, Z. anorg. Chem. 1894, 7, 209; Ramsay and Cundall, J.C.S. 1885, 47, 187; 1890, 57, 590, recommend acid of initial  $\rho$  1.5 as most suitable). The acid and arsenious oxide are carefully heated on a water bath in a large retort, or a flask with a splash-trap; the reaction may become violent. The gas is dried by calcium chloride and liquefied in a glass worm cooled in ice and salt. If  $\text{N}_2\text{O}_4$  is in excess a bluish-green liquid condenses, which on evaporating in a current of nitric oxide and reliquefying gives at  $-10^\circ$  an indigo-blue liquid, which is sealed up in a tube. Its ready dissociation into NO (b.p.  $-165^\circ$ ) and  $\text{N}_2\text{O}_4$  (b.p.  $22^\circ$ ) makes it difficult to remove the last trace of  $\text{N}_2\text{O}_4$ .

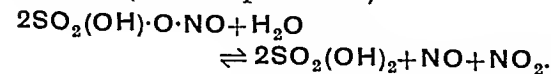
The reaction between  $\text{As}_2\text{O}_3$  and  $\text{HNO}_3$  is catalysed by small traces ( $<10^{-8}$  g.-mol. per l.) of mercuric ions, but retarded by larger amounts, and with  $7.7 \times 10^{-6}$  g.-mol. per l. it does not occur (Klemenc and Pollak, Z. anorg. Chem. 1921, 115, 131).

2. By passing an electric arc discharge through liquid air, when the  $\text{N}_2\text{O}_3$  remains suspended in the liquid air in the form of a flocculent green solid, resembling precipitated chromic hydroxide. On evaporation of the excess of liquid air it is left as a slightly blue amorphous powder, which melts at  $-111^\circ$  and assumes a deep blue colour, which persists after resolidification in liquid air (Helbig, Atti R. Accad. Lincei, 1903, [v], 12, 166; Fischer and Braehmer, Ber. 1906, 39, 940). In the region of the arc NO is formed, which in the boiling liquid air combines with oxygen to form  $\text{N}_2\text{O}_3$ . This reaction in favourable conditions may be quantitative, since  $\text{N}_2\text{O}_4$  is solid at temperatures below the dissociation temperature of  $\text{N}_2\text{O}_3$  and the latter is oxidised to  $\text{N}_2\text{O}_4$  only above  $-100^\circ$  (Scarpa, Gazzetta, 1907, 37, ii, 185).

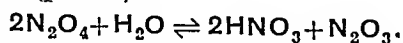
3. By reduction of liquid nitrogen peroxide with gaseous nitric oxide (Peligot, Ann. Chim. Phys. 1841, [iii], 2, 58; Lunge and Porschnow, l.c.). On saturation and subsequent cooling dark blue crystals of  $\text{N}_2\text{O}_3$  separate, m.p.  $-103^\circ$ , no other compound being formed. The eutectic mixture ( $\text{N}_2\text{O}_4$  63.6 and NO 36.4%), melts at  $-112^\circ$  (Wittorf, J. Russ. Phys. Chem. Soc. 1904, 36, 857; Z. anorg. Chem. 1904, 41, 85; Baume and Robert, Compt. rend. 1919, 169, 968).

4. By the action of 5-6N. nitric acid on copper; with more concentrated acid the gas contains an excess of  $\text{NO}_2$  (Priestley, quoted by Meldrum, J.C.S. 1933, 902; Bagster, *ibid.* 1921, 119, 82).

5. By the action of water on "chamber crystals" (nitrososulphuric acid):



6. By the action of water on liquid nitrogen peroxide (p. 526d):



*Properties.*—Nitrogen trioxide at ordinary temperatures is a brownish-red gas with a density corresponding with almost complete

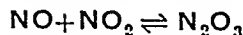
dissociation into NO and  $\text{NO}_2$ ; allowing for some polymerisation of  $\text{NO}_2$  to  $\text{N}_2\text{O}_4$ , the density shows that a little  $\text{N}_2\text{O}_3$  is also present in the gas (Ramsay and Cundall, *ibid.* 1890, 57, 590; Lunge and Porschnow, l.c.; Dixon and Poterkin, J.C.S. 1899, 75, 613; Wourtsel, Compt. rend. 1920, 170, 109). The absorption spectra of gaseous  $\text{N}_2\text{O}_3$  and  $\text{NO}_2$  are identical (Mosser, Ann. Phys. Chem. 1877, 10, 139). The blue liquid has no definite boiling-point, but at  $-21^\circ$  the composition is very close to  $\text{N}_2\text{O}_3$  (Francesconi and Sciacca, Gazzetta, 1904, 34, i, 447); from the vapour pressure curves between  $-80^\circ$  and  $35^\circ$  the boiling-point of pure  $\text{N}_2\text{O}_3$  would appear to be  $-27^\circ/760$  mm. (Baume and Robert, l.c.). After prolonged drying over phosphorus pentoxide the temperature of the liquid can be raised to  $43^\circ$  without any appearance of obullition (H. B. and M. Baker, J.C.S. 1912, 101, 2339). The density of the liquid at  $0^\circ$  is 1.4490 (Gauthier, Annalen, 1888, 245, 96; the specimen began to boil at  $3.5^\circ$ ).

Pure nitrogen trioxide exists only in the solid state at very low temperatures or in the liquid state under pressure of nitric oxide, and it dissociates above  $-100^\circ$ : it cannot be distilled in vacuum because of dissociation, but it might be possible to distil it under pressure in nitric oxide (Baume and Robert, l.c.).

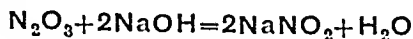
The specific magnetic susceptibility of the liquid is  $\chi = -0.21 \times 10^{-6}$  and of the solid  $\chi = -0.03 \times 10^{-6}$  (Soné, Sci. Rep. Tôhoku, 1922, 11, 139); the fact that it is diamagnetic suggests that, in spite of its intense colour, the substance consists of molecules  $\text{NO} \cdot \text{O} \cdot \text{NO}$  or  $\text{O}_2 \cdot \text{N} \cdot \text{NO}$ .

As usually prepared, liquid nitrogen trioxide mixes with water to form a blue-green liquid which above  $0^\circ$  evolves nitric oxide, and on dilution forms nitrous acid; according to Baker (l.c.), it is practically insoluble in water, in which it sinks, forming NO and  $\text{N}_2\text{O}_4$ , the latter dissolving in the water. With concentrated sulphuric acid nitrososulphuric acid (see p. 532b) is formed.

Oxygen does not react with nitrogen trioxide below  $-110^\circ$ . Above  $-100^\circ$   $\text{N}_2\text{O}_3$  is oxidised by oxygen to  $\text{N}_2\text{O}_4$  and below  $-150^\circ$   $\text{N}_2\text{O}_4$  is reduced by NO to  $\text{N}_2\text{O}_3$  (Francesconi and Sciacca, l.c.).  $\text{N}_2\text{O}_3$  oxidises metals, forming NO at low temperatures and nitrogen at higher temperatures. The gas is absorbed by alkalis and more rapidly than  $\text{NO}_2$ , a nitrito being formed, so that the equilibrium

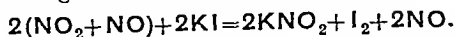


must be existent to some extent in the gas mixture, the  $\text{N}_2\text{O}_3$  being quickly renewed as it is absorbed:



(Lo Blanc, Z. Elektrochem. 1906, 12, 544). Liquid nitrogen trioxide is instantly absorbed by sodium hydroxide at  $-22^\circ$ , whilst liquid  $\text{N}_2\text{O}_4$  reacts only slowly (Foerster and Blich, Z. anorg. Chem. 1910, 23, 2017). Dry nitrogen trioxide is quantitatively absorbed by dry potassium hydroxide (Klinger, *ibid.* 1914, 27, 7). From a mixture of NO and  $\text{NO}_2$  only  $\text{NO}_2$

is absorbed by potassium iodide solution (Raschig and Prahl, *ibid.* 1929, 42, 253):



Nitrogen Dioxide,  $\text{NO}_2$ , and Dinitrogen Tetroxide,  $\text{N}_2\text{O}_4$  ("nitrogen peroxide" is the name commonly used for the *gaseous* equilibrium mixture:  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ ; Graham, "Elements of Chemistry," 1850, Vol. I, p. 344). This oxide can exist in the form  $\text{NO}_2$  only within narrow temperature limits: at low temperatures the polymer  $\text{N}_2\text{O}_4$  is the stable form, and at higher temperatures (above  $140^\circ$ )  $\text{NO}_2$  dissociates into  $\text{NO}$  and oxygen.

*Preparation*.—1. By oxidation of nitric oxide by oxygen:  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ . Dry gaseous  $\text{NO}$  and  $\text{O}_2$  in the volume ratio 2:1, well mixed by passing through a tube filled with glass or porcelain fragments, condense at  $-20^\circ$  to a colourless crystalline mass of  $\text{N}_2\text{O}_4$  (Dulong, *Ann. Chim. Phys.* 1816, [ii], 2, 317; Peligot, *ibid.* 1841, [iii], 2, 58). Similarly, the gas resulting from the action of concentrated nitric acid on arsenious oxide (p. 522*d*) is converted by excess of oxygen into  $\text{N}_2\text{O}_4$ .

Mandle and Russ (*Z. angew. Chem.* 1908, 21, 486) state that the rate and extent of union of  $\text{NO}$  and  $\text{O}_2$  is affected by the character of the oxygen; for example, electrolytic oxygen is more active after passing over heated palladium, and ozonisation retards the action. Holwech (*ibid.*, 2131) found that combination is practically complete, and the velocity of reaction the same, with oxygen from different sources.

According to Francesconi and Sciacca (*Gazzetta*, 1904, 34, i, 447), at liquid air temperature nitric oxide and oxygen form nitrogen tetroxide even if both are in the gaseous state, provided the temperature is below  $-110^\circ$ .

2. By passing nitric acid vapour through a heated tube:

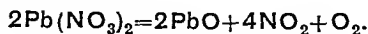


3. By the action of concentrated nitric acid on copper or bismuth:



The gas was discovered in this way in 1777 by Priestley ("Experiments and Observations on Different Kinds of Air," Birmingham, 1790, Vol. III, p. 115), who also obtained it by method (4). He called it "nitrous acid vapour," and made many interesting experiments with it.

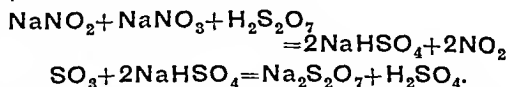
4. By heating dry lead nitrate in a hard glass tube and passing the gas (which may be dried by passing over calcium chloride) through a glass worm-tube cooled in a mixture of ice and salt to condense the nitrogen dioxide to liquid (Priestley, 1777; cf. Meldrum, *J.C.S.* 1933, 905; Dulong, *l.c.*):



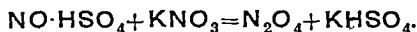
Copper nitrate (which cannot be dried without decomposition) decomposes similarly on heating. Alkali nitrates evolve  $\text{NO}_2$  when electrolysed in the fused state (Bogorodski, *J. Russ. Phys. Chem. Soc.* 1905, 37, 703).

5. By the action of fuming sulphuric acid on a homogeneous mixture of alkali nitrite and

nitrate made by fusing the salts together. sufficient  $\text{NaHSO}_4$  from a previous preparation is added to fix any free sulphur trioxide present (Winand, *G.P.* 193696, 1907):

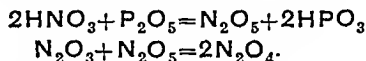


6. By warming nitrososulphuric acid (chamber crystals) with dry potassium nitrate (Girard and Pabst, *Bull. Soc. chim.* 1878, [ii], 30, 531; Park and Partington, *J.C.S.* 1924, 125, 72):



Sulphur dioxide is passed *slowly* into 100 c.c. of fuming nitric acid in a stoppered retort, well cooled in a good freezing mixture of ice and salt, until a pasty mass of chamber crystals forms. 240 g. of dry powdered  $\text{KNO}_3$  are added, the mixture stirred with a glass rod, and the retort gently heated on a water bath, the nitrogen peroxide being condensed in a worm-tube cooled in ice and salt.

7. By adding excess of phosphorus pentoxide to the blue liquid  $\text{N}_2\text{O}_3$  and then fuming nitric acid drop by drop till the liquid, kept well cooled in a freezing mixture, becomes yellow. The mixture is then distilled (Ramsay and Cundall, *J.C.S.* 1890, 57, 590; 1891, 59, 1076):



*Properties*.—Nitrogen peroxide at the ordinary temperature can exist as a dark orange-red corrosive gas with a peculiar unpleasant suffocating odour, and it is dangerously poisonous. At higher temperatures the colour of the gas first darkens, owing to dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$ , then at higher temperatures it becomes paler and finally colourless, owing to dissociation of  $\text{NO}_2$  into  $\text{NO}$  and oxygen. On cooling, the gas condenses to a dark orange-red liquid, boiling-point  $21.97^\circ$  (Thorpe and Rodger, *Phil. Trans.* 1895, 185, 451),  $21.2^\circ$  (Scheffer and Treub, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 536; *Z. physikal. Chem.* 1913, 81, 308) or  $21.9^\circ$  (Bousfield, *J.C.S.* 1919, 115, 45). The boiling-point is said to be raised by intensive drying (H. B. and M. Baker, *ibid.* 1912, 101, 2339). After drying by repeated distillation over phosphorus pentoxide for a period of 4–6 months the vapour pressure of nitrogen peroxide was *greater* than the normal value by as much as 25 mm. After a sudden change in temperature, the corresponding change in vapour pressure of the dry substance was established slowly, several hours being required to attain a steady value (Smits, *Z. physikal. Chem.* 1927, 129, 33; Smits, de Liefde, Swart, and Claassen, *J.C.S.* 1926, 2657). Stoddart (*ibid.* 1945, 448) found, however, that phosphorus pentoxide reacts with nitrogen peroxide to form a compound  $\text{P}_2\text{O}_5(\text{NO})_2$ , and the apparent increase of vapour pressure on drying is due to the oxygen evolved. The dried liquid has the normal vapour pressure. The colour of the liquid and its change with temperature are not affected by drying for several years over phosphorus pentoxide (Partington, unpublished), so that this does not seem to have any effect on

the equilibrium:  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  in the liquid state.

At  $10^\circ$  the liquid is pale yellow: it solidifies in a good freezing mixture (it supercools strongly) to a nearly colourless solid, melting-point  $-10.1^\circ$  (Ramsay, *ibid.* 1890, 57, 590; Z. physikal. Chem. 1890, 5, 221),  $-10.95^\circ$  (Bruni and Berti, Atti R. Accad. Lincei, 1900, 9, i, 321),  $-10.8^\circ$  (Scheffer and Treub, *l.c.*), or  $-10.5^\circ$  (Egerton, J.C.S. 1914, 105, 647). The critical temperature is  $158.2^\circ$  (Scheffer and Treub, *l.c.*) or  $158.4^\circ$  (Bennewitz and Windisch, Z. physikal. Chem. 1933, A, 166, 416), the critical pressure  $100 \pm 2$  atm. (Scheffer and Treub, *l.c.*), the critical density 0.570 g. per ml. (Bennewitz and Windisch, *l.c.*).

In the solid state at low temperatures this oxide probably consists entirely of colourless  $\text{N}_2\text{O}_4$ , and the liquid, except near the boiling-point, is also largely  $\text{N}_2\text{O}_4$ .

The vapour pressures of the liquid and solid have been investigated by Guye (J. Chim. phys. 1910, 8, 473), Scheffer and Treub (*l.c.*), and Egerton (*l.c.*); the latter gives:

Temperature, $^\circ\text{C}$ .	Pressure in mm.	Temperature, $^\circ\text{C}$ .	Pressure in mm.
-30	39.24	-70	0.151
-40	9.77	-80	0.036
-50	2.44	-90	0.0093
-60	0.605	-100	0.0023

and the formula:  $\log p = -1.3256/T + 3.354 \log T - 0.8950$  ( $p$  in mm. Hg,  $T$ =absolute temperature), is valid up to  $120^\circ$ .

Scheffer and Treub give for the solid and liquid (m.p.  $-10.8^\circ$ ):

Temperature, $^\circ\text{C}$ .	Pressure in mm.	Temperature, $^\circ\text{C}$ .	Pressure in mm.
-36.0	18	7.7	393
-23.0	53	15.0	565
-10.8	146	21.45	770
-6.9	180	27.4	1,007
-0.6	256	39.0	1,668
		43.2	1,982

Mittasch, Kuss, and Schleuter (Z. anorg. Chem. 1927, 159, 1) agree with Scheffer and Treub to  $40^\circ$  and between  $40^\circ$  and  $60^\circ$  the maximum deviation is 1.5% (see Fales and Shapiro, J. Amer. Chem. Soc. 1938, 60, 794).

The liquid has been used as a solvent for molecular weight determinations: the molecular elevation of boiling-point is  $13.7^\circ$  and the molecular depression of freezing-point is  $41^\circ$ , both for 100 g. of solvent (Ramsay, Z. physikal. Chem. 1890, 5, 221; Bruni and Berti, Gazzetta, 1900, 30, ii, 151; Frankland and Farmer, J.C.S. 1901, 79, 1356).

The liquid is not polymerised further than  $\text{N}_2\text{O}_4$ , and in acetic acid the maximum molecular weight corresponds with  $\text{N}_2\text{O}_4$  (Ramsay, *ibid.* 1888, 53, 621; Ramsay and Shields, *ibid.* 1893, 12, 433). The density of the liquid (Gauthier, Annalen, 1888, 245, 96) is:

$t^\circ\text{C}$ .	-5	-2	0	5	10	15
$\rho$ .	1.5035	1.5020	1.4935	1.4880	1.4770	1.4740

Thorpe (J.C.S. 1880, 37, 224) found 1.4903 at  $0^\circ$ , and Bousfield (*ibid.* 1919, 115, 45) found:

$t^\circ\text{C}$ .	0.08	7	11	15	18	20
$\rho$ .	1.4925	1.4770	1.4682	1.4591	1.4521	1.4475

and represented the specific volume (ml. per g.) by the equation:

$$v = 0.67027 + 0.0010075t + 0.000003t^2$$

whilst according to Thorpe (*l.c.*) 1 vol. at  $0^\circ$  becomes at

$t^\circ\text{C}$ .	5	10	15	20
	1.00789	1.01573	1.02370	1.03196

Pascal and Garnier (Bull. Soc. chim. 1919, [iv], 25, 309) find that the density of the liquid, between  $0^\circ$  and the boiling-point, at the temperature  $t$  can be represented by  $1.490 - 0.00215t$ .

The vapour density of the gas as determined by various experimenters is reviewed by Schrober (Z. physikal. Chem. 1897, 24, 651) who gives the following percentage dissociations of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  at 760 mm. pressure:

$27^\circ$	$66^\circ$	$103^\circ$	$150^\circ$	$199^\circ$
18.05	58.88	89.44	98.45	99.81

(above  $140^\circ$  some dissociation of  $\text{NO}_2$  into  $\text{NO}$  and  $\text{O}_2$  occurs).

The vapour densities are also represented by an equation due to J. Willard Gibbs ("Scientific Papers," 1906, Vol. I, p. 378; J. R. Partington, "Chemical Thermodynamics," Constable, 1940, p. 99):

$$\log \frac{1.589(D-1.589)}{(3.178-D)^2} = \frac{3.118.6}{273+t^\circ\text{C}} + \log p_{\text{mm}} - 12.451$$

where  $D$ =vapour density (air=1). The percentage dissociation at the boiling-point ( $21.9^\circ$ ) calculated from this equation is 15.7.

At  $64^\circ$  and 1 atm. pressure one half of the  $\text{N}_2\text{O}_4$  is dissociated and at  $150^\circ$  dissociation into  $\text{NO}_2$  is complete. Above  $140^\circ$  decomposition of  $\text{NO}_2$  into  $\text{NO}$  and oxygen takes place:  $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ , this change being practically complete at  $620^\circ$ . At  $184^\circ$ , 5%, and at  $494^\circ$ , 56.5%, of the  $\text{NO}_2$  is dissociated (Richardson, J.C.S. 1887, 51, 397; Bodenstein and Katayama, Z. Elektrochem. 1909, 15, 244). The dissociation  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  in solution in chloroform has also been investigated (Cundall, J.C.S. 1891, 59, 1076; Ostwald, *ibid.* 1892, 61, 242; for solutions in carbon tetrachloride, see Coon, J. Amer. Chem. Soc. 1937, 59, 1910).  $\text{NO}_2$  is dissociated by an electric glow discharge (Zeunck and Strasser, Physikal. Z. 1911, 12, 1201).

The specific heat of gaseous nitrogen peroxide (Berthelot and Ogier, Ann. Chim. Phys. 1883, [v], 30, 382) is anomalous, since it includes the heat of dissociation of  $\text{N}_2\text{O}_4$  (Swart, Z. physikal. Chem. 1891, 7, 120). This may be subtracted to give the true specific heat (McCullum, J. Amer. Chem. Soc. 1927, 49, 28) as follows:

$t^\circ\text{C}$ .	33.73	60.9	97.51	120	150	160
$C_p$ obs. g.-cal. per g. mol.	126	178	93	49.2	26.3	24.2
$C_p$ true g.-cal. per g.-mol.	11.4	14.7	17.5	19.0	10.4	10.5

The heat of formation of gaseous nitrogen peroxide (which is endothermic) is  $\frac{1}{2}\text{N}_2 + \text{O}_2$

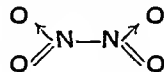
$=\text{NO}_2-8,125$  g.-cal.;  $\text{NO}+\frac{1}{2}\text{O}_2=\text{NO}_2+13,450$  g.-cal.;  $\text{N}_2+2\text{O}_2=\text{N}_2\text{O}_4-2,650$  g.-cal.;  $2\text{NO}_2+\text{O}_2=\text{N}_2\text{O}_4+40,500$  g.-cal. (J. Thomsen, "Thermochemistry," trans. by K. A. Burke, Longmans, 1908, p. 252); the heat of dissociation is  $\text{N}_2\text{O}_4=2\text{NO}_2-13,600$  g.-cal. (Thomsen) or  $-13,960$  g.-cal. (Verhoek and Daniels, J. Amer. Chem. Soc. 1931, 53, 1186). The heat of formation of liquid  $\text{N}_2\text{O}_4$  is  $-4,000$  g.-cal. and the latent heat of evaporation is  $4,330$  g.-cal. per g.-mol. (Berthelot, Ann. Chim. Phys. 1875, [v], 6, 145). The latent heat of fusion is  $33.7$  g.-cal. per g. (from the freezing-point depression) and the specific heat of the liquid from the melting-point to  $33^\circ$  is  $0.477$  g.-cal. per g. (Ramsay, Z. physikal. Chem. 1890, 5, 221; J.C.S. 1890, 57, 590). The thermal conductivity of the gas is anomalous owing to dissociation and varies with temperature and pressure (Feliciani, Physikal. Z. 1905, 6, 20); it reaches a high maximum value at  $65^\circ$ . The refractive index of the vapour at  $36^\circ$  is  $1.000503$  (Dulong, q. in Z. physikal. Chem. 1901, 36, 332) or  $1.000509$  for  $\text{NO}_2$  and  $1.001123$  for  $\text{N}_2\text{O}_4$  for  $\lambda=664$  m $\mu$ . (C. and M. Cuthbertson, Proc. Roy. Soc. 1913, 89, 361). The gas shows a strong orange or yellowish-green fluorescence (Norris, J.C.S. 1929, 1604). The absorption spectrum has often been investigated (e.g., by Hautefeuille and Chappuis, Compt. rend. 1881, 92, 80; 1882, 94, 946; Herzberg, Z. physikal. Chem. 1930, B, 10, 189).

The surface tension of the liquid is  $26.56$  dynes per cm. at  $19.8^\circ$  (Ramsay and Shields, J.C.S. 1893, 63, 1099) and the viscosity  $4.720 \times 10^{-3}$  dyne-sec./cm.<sup>2</sup> at  $9.15^\circ$ , and  $4.401$  dyne-sec./cm.<sup>2</sup> at  $15.36^\circ$  (Thorpe and Rodger, Phil. Trans. 1895, 185, 397; Batchinski, Z. physikal. Chem. 1913, 84, 658). Nitrogen peroxide gas does not conduct electricity and the liquid conducts only slightly. The dielectric constant of the vapour varies with temperature and pressure (Bädeker, *ibid.* 1901, 36, 305; Zahn, Physikal. Z. 1933, 34, 461); the results indicate that both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  have small dipole moments, but it is not certain which is greater (Williams, J. Amer. Chem. Soc. 1934, 56, 1427; Schutz, Z. Physik, 1938, 109, 517). The specific magnetic susceptibility of the liquid ( $\text{N}_2\text{O}_4$ ) at  $-16^\circ$  is  $\chi=-0.26 \times 10^{-6}$  (Soné, Sci. Rep. Tôhoku, 1922, 11, 139);  $\text{NO}_2$  has an odd electron and is paramagnetic, and Havens (Physical Rev. 1932, [ii], 41, 337) finds the specific susceptibility  $0.375$  that of oxygen; Soné (*l.c.*) found  $\chi=+4.5 \times 10^{-6}$  at  $20^\circ$ .

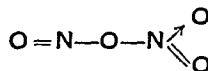
There is some doubt as to the shape of the  $\text{NO}_2$  molecule; Bailey and Cassie (Nature, 1933, 131, 239) and Maxwell, Mosley, and Deming (J. Chem. Phys. 1934, 2, 331) conclude that it is linear and symmetrical, but Penney and Sutherland (Nature, 1935, 136, 146) that it is bent, the angle being  $110-120^\circ$ , or  $140^\circ$ . The electronic structure is probably a resonance hybrid with a three-electron bond (p.519a)  $:\ddot{\text{O}}:\text{N}::\ddot{\text{O}}:$  and  $\ddot{\text{O}}::\text{N}:\ddot{\text{O}}:$  (Pauling, J. Amer. Chem. Soc. 1931, 53, 3225; Noyes, Z. Elektrochem. 1931, 37, 569), and the odd electron is probably responsible for the ready formation of compounds with metallic chlorides (Besson, Compt. rend. 1889,

108, 1012; Reihlen and Hake, Annalen, 1927, 452, 47).

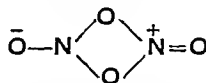
The structure of  $\text{N}_2\text{O}_4$  has been represented as



$\text{O}=\text{N}-\text{O}-\text{O}-\text{N}=\text{O}$ , and

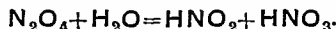


(Divers, J.C.S. 1885, 47, 630; 1904, 85, 110; Wieland, Ber. 1921, 54 [B], 1776; Battagay and Kern, Bull. Soc. chim. 1927, [iv], 41, 1336; Hendricks, Z. Physik, 1931, 70, 699), but the first formula, with a bond between the two nitrogen atoms, is probably correct (Giauque and Kemp, J. Chem. Phys. 1938, 6, 40); Longuet-Higgins (Nature, 1944, 153, 408, 459) proposed a formula with an oxygen bridge:

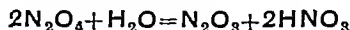


Nitrogen dioxide gas supports the combustion of burning carbon, sulphur, and phosphorus; carbon monoxide burns to carbon dioxide, and hydrogen sulphide to sulphur, with simultaneous formation of nitric oxide. A mixture of the gas with hydrogen forms ammonia when passed over heated platinum (Kuhlmann, Annalen, 1839, 29, 272), the reaction being violent and sometimes explosive, or when passed over reduced nickel or copper (Sabatier and Senderens, Compt. rend. 1902, 135, 278). Potassium burns in the gas or in contact with the slightly moist liquid with a red flame; sodium reacts at the ordinary temperature without ignition; many metals and lower oxides are oxidised by the gas at  $500^\circ$ : sodium, potassium, mercury, and lead form nitrates with production of  $\text{NO}$  (Sabatier and Senderens, Ann. Chim. Phys. 1896, [vii], 7, 348). Additive compounds are formed with many metallic salts, etc., e.g.,  $\text{FeCl}_3\text{NO}_2$ ,  $\text{SnCl}_4\text{NO}_2$ , etc. (Weber, Ann. Phys. Chem. 1863, [ii], 118, 471; 1864, [ii], 123, 347; Besson, Compt. rend. 1889, 108, 1012; Bull. Soc. chim. 1889, [iii], 1, 771; Reihlen and Hake, Annalen, 1927, 452, 47; Thomas, Ann. Chim. Phys. 1898, [vii], 13, 145), and with unsaturated organic compounds.

With water,  $\text{N}_2\text{O}_4$  behaves as a mixed anhydride, forming nitrous and nitric acids:



With a small quantity of cold water (or better, with ice) the reaction:



occurs, two liquid layers being formed. The lower, deep-blue, layer is rich in  $\text{N}_2\text{O}_3$ . Further dilution converts the  $\text{N}_2\text{O}_3$  into nitrous acid, which on rise of temperature decomposes with evolution of nitric oxide:



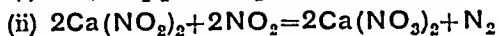
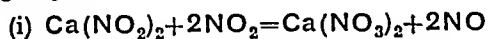
(Fritsche, J. pr. Chem. 1840, [i], 19, 179; 1841, [i], 22, 14; Schönbein, Ann. Physik, 1848, 73,

326; Odde, *Gazzetta*, 1915, 45, i, 413; Lowry and Lemen, *J.C.S.* 1936, 1, 6; Lowry, Lloyd, and Lloyd, *ibid.*, p. 10).

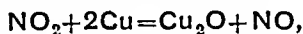
Aqueous alkalis form a mixture of nitrite and nitrate



the gas being more slowly absorbed than an equimolecular mixture of NO and NO<sub>2</sub>, which forms only nitrite (Foerster and Koch, *Z. angew. Chem.* 1908, 21, 2161). Barium oxide, BaO, reacts with incandescence at 200° to form a mixture of nitrite and nitrate (Dulong, *Ann. Chim. Phys.* 1816, [ii], 2, 317). Calcium oxide reacts up to 400° to form calcium nitrate and nitrite, nitric oxide, and nitrogen. The free nitrogen arises from the oxidation of calcium nitrite to nitrate, which may occur in the following ways:

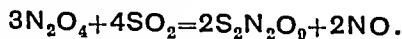


(Partington and Williams, *J.C.S.* 1924, 125, 947). Nitrogen peroxide reacts with finely divided copper to form cuprous oxide:

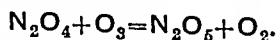


which then adsorbs an excess of NO<sub>2</sub>. Cuprous oxide in the cold takes up about 30% by weight of nitrogen peroxide gas without change in appearance, evolution of heat or other sign of chemical change. The product of the action of nitrogen peroxide on copper or cuprous oxide dissociates completely on heating, without reduction of the nitrogen peroxide; it reacts violently with water yielding nitric oxide and a solution of cupric nitrate with a little nitrite. At 65–70°, an inert solvent such as carbon tetrachloride removes the whole of the nitrogen peroxide, leaving a residue of cuprous oxide. The peroxide is adsorbed by and not chemically combined with the cuprous oxide (Park and Partington, *ibid.* 1924, 125, 72, 663; Klemene and Schroth, *Ber.* 1925, 58 [B], 168), and the so-called "nitro-copper," Cu<sub>2</sub>NO<sub>2</sub>, said to be formed (Sabatier and Senderens, *Compt. rend.* 1892, 115, 236; 1893, 116, 756), is merely the adsorption complex.

In the liquid state nitrogen peroxide and sulphur dioxide react to form nitrosyl disulphate, S<sub>2</sub>N<sub>2</sub>O<sub>6</sub> (see p. 532d):



Liquid ammonia reacts explosively with solid N<sub>2</sub>O<sub>4</sub> at –80°, but a current of gaseous ammonia led over the solid at –20° reacts less vigorously, the products being NO, nitrogen, ammonium nitrate, and water, with a trace of ammonium nitrite (Besson and Rosset, *ibid.* 1906, 142, 633). Dry oxygen does not oxidise N<sub>2</sub>O<sub>4</sub>, but ozone converts it into nitrogen pentoxide (Helbig, *Atti R. Accad. Lincei*, 1902, 11, ii, 311; 1903, 12, i, 211; *Z. Elektrochem.* 1906, 12, 550; Foerster and Koch, *Z. angew. Chem.* 1908, 21, 2216):



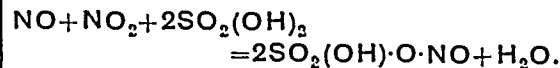
In presence of water, oxygen and oxidising agents convert N<sub>2</sub>O<sub>4</sub> into nitric acid (see p. 572a).

Nitrogen peroxide dissolves in dilute and concentrated nitric acid; with concentrated acid a yellow "fuming nitric acid" is formed (Lunge, *Ber.* 1879, 12, 1058; Bousfield, *J.C.S.* 1919, 115, 45). The density of the nitric acid is markedly increased (Lunge and Marchlewsky, *Z. angew. Chem.* 1892, 5, 10), reaching a maximum when the solution contains 42.5% by weight of the peroxide, corresponding with the composition N<sub>2</sub>O<sub>5</sub>.N<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O, this solution being stable at –48.5°, above which temperature it dissociates (Pascal and Garnier, *Bull. Soc. chim.* 1919, [iv], 25, 309).

Liquid N<sub>2</sub>O<sub>4</sub> forms dangerously explosive solutions in liquid hydrocarbons (*v. Explosives*, Vol. IV, 545d).

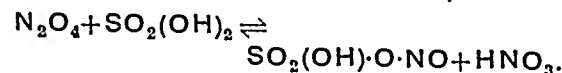
Pure nitrogen peroxide does not react with cold aromatic hydrocarbons. With benzene at 80° the main products are 1:3:5-trinitrobenzene and picric acid. Nitrobenzene is indifferent at 80°. Phenol dissolved in a cold mixture of benzene and light petroleum is readily nitrated to *o*- and *p*-nitrophenol. *o*-Cresol gives *o*- and *p*-nitro-*o*-cresol; *m*-cresol yields *o*- and *p*-nitro-*m*-cresol, whilst the *p*-compound gives *o*-nitro-*p*-cresol and *o*-dinitro-*p*-cresol. 1:3:4 *m*-Xylenol is converted into the corresponding 5-nitro-compound. *α*-Naphthol gives a mixture of 2-nitro-*α*-naphthol and 2:4-dinitro-*α*-naphthol. Acetanilide in ethereal solution is transformed into benzenediazonium nitrate. Diphenylamine in ethereal solution yields diphenylnitrosamine; in benzene solution it gives *p*-nitrodiphenylnitrosamine. A consideration of these reactions leads to the formula O<sub>2</sub>N·NO<sub>2</sub> as the most probable constitution of nitrogen peroxide, which is also in accord with its other reactions and with the more convincing direct structural determination (p. 526c); its decomposition by alkali is then analogous to that of other symmetrically-paired atoms or radicals, *e.g.*, cyanogen to cyanide and cyanate, chlorine to chloride and hypochlorite (Wieland, *Ber.* 1921, 54 [B], 1776).

NO<sub>2</sub> may be determined in presence of excess of NO by absorption in potassium iodide solution (p. 523d) or by shaking the gas with concentrated sulphuric acid, which absorbs equimolecular amounts of each gas:



The "N<sub>2</sub>O<sub>3</sub>" content of the acid is then determined in a Lunge nitrometer, an allowance being made for the solubility of NO in the acid. The excess of NO in the residual gas is absorbed by acid potassium bromate solution, and the nitric acid formed is determined in the nitrometer (Klemene and Muha, *Z. anorg. Chem.* 1924, 134, 1208).

Nitrogen peroxide is absorbed by concentrated sulphuric acid to form a mixture of nitrososulphuric and nitric acids, the reaction being reversible (Lunge, *Ber.* 1879, 12, 1058):

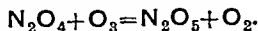


The iso-dinitrogen tetroxide supposed by Raschig (*Chem.-Ztg.* 1907, 31, 359; *Z. anorg. Chem.* 1913, 84, 115) to be formed as one of the

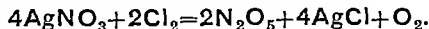
first products in the reaction between nitric oxide and air has no existence, the product being nitrogen peroxide.

Nitrogen Pentoxide or Nitric Anhydride,  $N_2O_5$ , was discovered by Deville in 1849. It is prepared as follows:

1. By oxidising cooled liquid nitrogen peroxide with ozonised oxygen (Helbig, Atti R. Accad. Lincei, 1903, [v], 12, i, 211; Z. Elektrochem. 1906, 12, 550; Foerster and Koch, Z. angew. Chem. 1908, 21, 2216):



2. As first prepared by Deville (Ann. Chim. Phys. 1850, [iii], 28, 241; Rice and Getz, J. Physical Chem. 1927, 31, 1572) by passing dry chlorine over silver nitrate at 50–60°, the  $N_2O_5$  in the gaseous product being condensed in a tube cooled in a freezing mixture:



3. Most conveniently, as first prepared by Weber (J. pr. Chem. 1872, [ii], 6, 342; Berthelot, Bull. Soc. chim. 1874, [ii], 21, 53; Ann. Chim. Phys. 1875, [v], 6, 202; Meyer, Ber. 1889, 22, 23; Gibson, Proc. Roy. Soc. Edin. 1908, 28, 705), by dehydrating pure concentrated nitric acid with phosphorus pentoxide, with constant cooling, and then distilling the nitrogen pentoxide formed. The syrupy liquid formed from the nitric acid and phosphorus pentoxide is poured into a dry retort and distilled into a receiver surrounded by a freezing mixture. The orange-red distillate separates into two layers, the upper of which is cooled in ice. The crystals formed are drained, again melted and crystallised, and drained from the mother-liquor.

The operation is facilitated by performing the distillation in a current of ozonised oxygen, which prevents decomposition into oxygen and lower oxides of nitrogen. To remove the last trace of moisture the gas is passed through a long tube containing phosphorus pentoxide and the nitrogen pentoxide is then almost completely condensed by cooling at  $-80^\circ$  (Russ and Pokorný, Monatsh. 1913, 34, 1051; Daniels and Bright, J. Amer. Chem. Soc. 1920, 42, 1131). The possibility of explosion should be provided for.

Pure nitrogen pentoxide forms glistening white rhombic crystals, density 1.99 at  $16^\circ$  (Soné, Sci. Rep. Tôhoku, 1922, 11, 139). According to Berthelot the melting-point is  $29.5^\circ$ , but Russ and Pokorný (*l.c.*) say that when pure it has no true melting-point, liquefaction being due to traces of impurities, but it sublimates at about  $34^\circ$ . The liquid boils with decomposition into  $N_2O_4$  and oxygen at about  $45^\circ$ , after previously darkening in colour. The crystals (slightly impure) become yellow some time before melting; at the melting-point they are orange, turning dark brown as the temperature rises. The vapour pressure of the pure solid is given by the formula (Daniels and Bright, *l.c.*):

$$\log p = 1.244/T + 34.1 \log T - 85.929$$

( $p$  mm. Hg,  $T$ =absolute temperature). The calculated molar heat of fusion is 8,280 g.-cal. per g.-mol., and the calculated molar heat of evaporation 4,840 g.-cal. per g.-mol. The heats

of sublimation calculated for various absolute temperatures (Daniels and Bright, *l.c.*) are:

$T^\circ K.$	263	273	283	293
G.-cal. per g.-mol.	12,360	12,760	13,360	14,140

The heat of formation of solid  $N_2O_5$  is 11,900 g.-cal. per g.-mol., hence that of gaseous  $N_2O_5$  is  $-1,200$  g.-cal. per g.-mol. (Berthelot, Ann. Chim. Phys. 1875, [v], 6, 171; Compt. rend. 1880, 90, 783). The heat of reaction,



is 2,300 g.-cal. evolved, and with excess of water,  $N_2O_5 + Aq. = 2HNO_3, Aq.$ , is 16,680 g.-cal. (Berthelot, *l.c.*). The specific magnetic susceptibility of the solid at  $16^\circ$  is  $\chi = -0.33 \times 10^{-6}$  (Soné, Sci. Rep. Tôhoku, 1922, 11, 139).

According to Deville the crystals can be kept without decomposition in diffuse daylight below  $8^\circ$ , but in sunlight at  $25^\circ$  the solid melts and undergoes explosive decomposition into nitrogen peroxide and oxygen. A trace of ozone retards the thermal decomposition, but the rate of thermal decomposition is not affected by the presence of chlorine, bromine (which retards the photochemical decomposition), carbon monoxide or hydrogen, whilst carbon disulphide increases the rate of decomposition (Daniels, Wulf, and Karrer, J. Amer. Chem. Soc. 1922, 44, 2402; Busse and Daniels, *ibid.* 1927, 49, 1257). Reducing the pressure of the vapour does not retard the decomposition, but below a critical pressure of about 0.25 mm. the reaction velocity begins to increase, attaining finally, at the lowest pressure, five-times the normal value (Hirst and Rideal, Proc. Roy. Soc. 1925, 109, 526). The decomposition at all temperatures investigated is a unimolecular homogeneous reaction, hence it may occur as  $N_2O_5 = N_2O_3 + O_2$ , followed by a rapid reaction  $N_2O_3 + N_2O_5 = 2N_2O_4$  (Daniels and Johnston, J. Amer. Chem. Soc. 1921, 48, 53; Hirst, J.C.S. 1925, 127, 657; White and Tolman, J. Amer. Chem. Soc. 1925, 47, 1240; Hunt and Daniels, *ibid.*, p. 1602; Rice and Getz, J. Physical Chem. 1927, 31, 1572). In illuminated  $NO_2$  an equilibrium  $2NO_2 \rightleftharpoons 2NO + O_2$  is set up, and in the photochemical decomposition of  $N_2O_5$  the  $NO_2$  may first form  $NO$  which then reacts with  $N_2O_5$  to form  $3NO_2$  (Norris, J.C.S. 1927, 761). The velocity coefficient of the decomposition of  $N_2O_5$  in carbon tetrachloride solution is the same as in the gas (Lueck, J. Amer. Chem. Soc. 1922, 44, 757).

$N_2O_5$  dissolves with a hissing noise in water to form nitric acid. It forms a solid crystalline compound  $N_2O_5 \cdot 2HNO_3$  on cooling a solution of  $N_2O_5$  in concentrated nitric acid. Phosphorus and potassium burn in the liquid pentoxide if slightly warmed; charcoal does not decompose it even on boiling, but burns brilliantly if previously ignited.  $N_2O_5$  dissolves in freshly distilled and fused sulphur trioxide, giving an almost quantitative yield of  $N_2O_5 \cdot 4SO_3$ , m.p.  $124-125^\circ$ , b.p.  $218-220^\circ$ , also formed as a crystalline precipitate on mixing solutions of the two oxides in carbon tetrachloride (Pictet and Karl, Compt. rend. 1907, 145, 238).

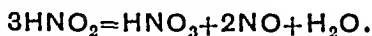
Nitrogen Hexoxide.—Hautefeuille and Chappuis (*ibid.* 1881, 91, 762; 1881, 92, 80, 134;



1882, 94, 946, 1111, 1306), and Berthelot (Bull. Soc. chim. 1881, [ii], 35, 227; Ann. Chim. Phys. 1881, [v], 22, 432), by the action of a silent discharge on a mixture of oxygen and nitrogen, obtained a gas with a characteristic absorption spectrum, and on cooling to  $-23^{\circ}$  a small quantity of a very volatile crystalline powder separated, supposed to be  $N_2O_6$ . The same spectrum was observed by Warburg and Leit-häuser (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1907, 229) with a mixture of ozone and  $N_2O_5$  vapour at  $0-18^{\circ}$ .

Schumacher and Sprenger (Z. physikal. Chem. 1928, 136, 77; 1929, B, 2, 267; Z. angew. Chem. 1929, 42, 697) and Lowry and Lemon (Nature, 1935, 135, 433; J.C.S. 1935, 692) supposed that  $NO_3$  is formed from  $N_2O_5$  vapour and ozone, and Schwarz and Achenbach (Ber. 1935, 68 [B], 343) claimed to have obtained it as a white solid, stable only below  $-142^{\circ}$ , by the action of an electric discharge on a mixture of  $NO_2$  and oxygen at low pressure in a special apparatus, but Klemenc and Noumann (Z. anorg. Chem. 1937, 232, 217) were unable to repeat the experiment, although they inferred from the absorption spectrum that  $NO_3$  may be formed in the evaporation of a liquid mixture of  $N_2O_4$  and ozone.

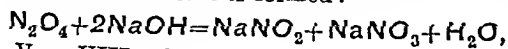
**Nitrous Acid,  $HNO_2$ .**—Nitrous anhydride ( $N_2O_3$ ) dissolves in excess of ice-cold water to form a dilute solution of nitrous acid. This is unstable (Knox and Reid, J.S.C.I. 1910, 38, 105T) although its salts and esters are comparatively stable. A solution of nitrous acid is formed on acidification of a dilute solution of a nitrite, and (free from metallic salt) by precipitating a solution of silver nitrite with dilute hydrochloric acid, or a solution of barium nitrite with dilute sulphuric acid. The solution contains some  $N_2O_3$  (which colours it blue) and readily evolves nitric oxide:



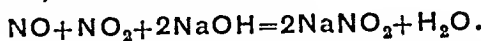
**Nitrites** are found to some extent in nature and are said to occur in the sap of some plants or to be formed when plant extracts are exposed to air (Mazé, Compt. rend. 1912, 155, 781; Bach, Biochem. Z. 1913, 52, 418; Klein, Bied. Zentr. 1915, 44, 162). The presence of nitrites in the atmosphere is established (Schönbein, Chem. News, 1862, 6, 241; Warrington, J.C.S. 1881, 39, 229; Hayhurst and Pring, *ibid.* 1910, 97, 868; Rae and Dhar, Z. anorg. Chem. 1931, 199, 422; Vorländer and Goldes, Ber. 1931, 64 [B], 1776; Wulf, J. Opt. Soc. Amer. 1935, 25, 231). They have been supposed to be formed from nitrates in solution by the action of sunlight (Moore, Proc. Roy. Soc. 1918, B, 90, 158; J.C.S. 1921, 119, 1555) and in photochemical assimilation (Baudisch and Mayor, Z. physiol. Chem. 1914, 89, 175).

Most nitrites are soluble in water and many in alcohol, but silver (3.2 g. per l.), bismuthyl, and basic lead nitrites are only sparingly soluble in water.

Alkali and alkaline earth hydroxides and carbonates absorb  $NO_2$  and  $N_2O_3$  (i.e., mostly  $NO + NO_2$ ; see p. 523b); with  $NO_2$  a mixture of nitrite and nitrate is formed:



whilst with  $N_2O_3$ , if  $NO$  is present in slight excess, practically pure nitrite is formed (Gay-Lussac, Ann. Chim. Phys. 1816, [ii], 1, 394; Divers, J.C.S. 1899, 75, 85):



Oxides of nitrogen as produced, e.g., by the action of an electric discharge on air or by the oxidation of ammonia, may be kept at  $300^{\circ}$  until absorbed by alkali, when practically only nitrite is formed (Badische Anilin- u. Soda-Fabrik, G.P. 188188, 1906).

Solid ammonium nitrite is formed by evaporating a concentrated solution of ammonium chloride and sodium nitrite in vacuum and subliming in vacuum (Rây, J.C.S. 1900, 95, 345; Neogi and Adhicary, *ibid.* 1911, 99, 116), or by passing the red gas ( $NO + NO_2$ ) from nitric acid and arsenious oxide (p. 522d) over lumps of solid ammonium carbonate in a cooled tube, dissolving in alcohol, and precipitating with ether (Sørensen, Z. anorg. Chem. 1894, 7, 33).

Many nitrates are reduced to nitrites on fusion with lead, copper, carbon (Fischer, Ann. Physik, 1849, 74, 115), sulphites (Étard, Bull. Soc. chim. 1877, [ii], 27, 434), and sulphur or barium sulphide (Roy, Compt. rend. 1889, 108, 1251), and in solution by reduction with sodium, potassium, calcium, and other metals (Schönbein, J. pr. Chem. 1868, [i], 105, 198) or by electrolytic reduction (Müller and Weber, Z. Elektrochem. 1903, 9, 955, 978; Müller and Spitzer, *ibid.* 1905, 11, 509; Ber. 1905, 38, 1190), silver being the best cathode material, when reduction to nitrite is almost complete before further reduction to ammonia occurs; with a copper anode the yield is then almost quantitative.

Nitrites are said to be formed by oxidising ammonia with hydrogen peroxide (Weith and Weber, Ber. 1874, 7, 1745; Hoppe-Seyler, *ibid.* 1883, 16, 1917), but this is probably incorrect (Traube, *ibid.* 1882, 15, 2432; Hodgkinson and Bellairs, Proc. C.S. 1895, 11, 9).

In the oxidation of copper in ammonia solution in contact with air (p. 499a) some ammonia is oxidised to nitrite (Schönbein, J. pr. Chem. 1857, [i], 70, 129; 1858, [i], 75, 73; Peligot, Compt. rend. 1858, 47, 1034; Berthelot, Ann. Chim. Phys. 1864, [iv], 1, 381). Ammonia is oxidised to nitrite and finally to nitrate by electrolytic oxidation of a solution containing sodium hydroxide and copper hydroxide with an anodic current density of 0.02–0.06 amp. per sq. cm., almost all the anode oxygen being used up (Traube and Biltz, Ber. 1904, 37, 3130; 1906, 39, 166).

The only practical method for the preparation of pure alkali and alkaline-earth nitrites is by double decomposition of the chlorides with silver nitrite (Oswald, Ann. Chim. 1914, [ix], 1, 32). Nitrites may be prepared by the action of sodium or potassium nitrite on the metallic acetates in presence of ammonium acetate, with ammonia, alcohol or acetone as solvent (Duval, Compt. rend. 1926, 182, 1150). Sodium nitrite is formed on heating the nitrate with some oxides, the best results being obtained with barium oxide or manganese dioxide (Taccchini, Giorn. Chim. Ind. Appl. 1924, 6, 275). Triple



nitrites of cobalt, nickel or copper with an alkali metal and mercury or a metal of the cerium or yttrium group are described (Cuttica *et al.*, *Gazzetta*, 1922, 52, ii, 270, 279; 1923, 53, i, 185, 374).

**Properties.**—Nitrous acid is a fairly strong acid, its dissociation constant being  $K = \frac{[H^+][NO_2^-]}{[HNO_2]} = 3.2 \times 10^{-4}$  at  $0^\circ$  and  $4.9 \times 10^{-4}$  at  $18^\circ$  (Reinders and Vles, *Rec. trav. chim.* 1925, 44, 1; Klemenc and Hayek, *Monatsh.* 1929, 53–54, 407. Rây, Dey, and Ghosh, *J.C.S.* 1917, 111, 413, found  $6.5 \times 10^{-4}$ , Schumann, *Ber.* 1900, 33, 527, found  $4.5 \times 10^{-4}$ , and Blanchard, *Z. physikal. Chem.* 1902, 41, 681, found  $4 \times 10^{-4}$ ). It is, however, slowly displaced from solutions of its salts by carbonic acid (Moore, *J. Amer. Chem. Soc.* 1904, 26, 959).

The equivalent conductivity at  $0^\circ$ C. and dilutions of  $v$  l. per g.-mol. is (Rây, Dey, and Ghosh, *l.c.*; cf. Schumann, *l.c.*; Ley and Kissel, *Ber.* 1899, 32, 1357):

$v$	32	64	128	256	1,024	$\infty$
$\Lambda$ ohm $^{-1}$	33.5	45.8	62.0	82.5	138	271

The mobility of the nitrite ion  $NO_2^-$  in dilute solution is (Klemenc and Hayek, *l.c.*; cf. Pick, *Dissert.*, Breslau, 1906; Vogel, *Z. anorg. Chem.* 1903, 35, 385):

$0^\circ$	$44.0$	$12.5^\circ$	$58.0$	$30^\circ$	$77$
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The heat of neutralisation of nitrous acid with baryta is 10,600 g.-cal. and with ammonia 9,100 g.-cal. (Berthelot, *Ann. Chim. Phys.* 1875, [v], 6, 145). The heat of formation (J. Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882, Vol. II, p. 199) is:



The decomposition of nitrous acid in solution:



occurs slowly in the cold when the liquid is quiescent; it is accelerated in contact with rough surfaces (sand, fragments of glass, etc.) and on shaking. The kinetics of the decomposition have been investigated by Rây, Dey, and Ghosh (*l.c.*) who found the following unimolecular velocity coefficients  $k$  in approximately 0.1% solution:

$0^\circ$	$21^\circ$	$40^\circ$
0.00014	0.00022	0.00057

Actually,  $k$  increases with the initial concentration of  $HNO_2$ , and there is a critical concentration above which decomposition is very rapid and below which it is very slow. This is, apparently, due to the secondary reactions: (a)  $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$  in solution and (b)  $N_2O_3 \rightleftharpoons NO + NO_2$  in the gas phase (Taylor, Wignall, and Cowley, *J.C.S.* 1927, 1923).

The reaction  $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$  is reversible and the equilibrium constant  $K = \frac{[HNO_3][NO]^2}{[H^+][NO_2^-]^3}$  has been determined (Saposhnikov, *J. Russ. Phys.-Chem. Soc.* 1901, 33, 506; Lewis and Edgar, *J. Amer. Chem. Soc.* 1911, 33, 292; Abel and Harasty, *Z. anorg. Chem.* 1924, 139, 1; Abel and Schmid, *Z. physikal. Chem.* 1928, 132, 55; Abel *et al.*, *ibid.*

1930, 148, 337; *Z. Elektrochem.* 1930, 36, 692; Klemenc and Hayek, *Z. anorg. Chem.* 1930, 186, 181). Lewis and Edgar found  $K = 0.0267$  at  $25^\circ$  and one atmosphere pressure of  $NO$ , but it varies with the nitric acid concentration. Klemenc and Hayek calculate for infinite dilution:

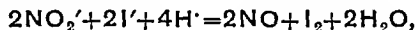
$t^\circ$	0	12.5	15	25	30	35
$1/K$	5.0	13.3	14.45	19.3	39.6	51

For finite concentrations the activities must be used instead of concentrations.

The acid is more stable in a compressed atmosphere of nitric oxide, and this has been applied in diazotisation reactions (Briner and Jonas, *Helv. Chim. Acta*, 1920, 3, 366).

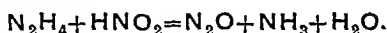
Nitrous acid is oxidised to nitric acid by the usual oxidising agents; its oxidation by hydrogen peroxide and subsequent precipitation of this with "nitron" acetate is used as a method of determination (Busch, *Ber.* 1906, 39, 1401; *v.* also this Vol., p. 589a), and nitrites are precipitated by 2,4-diamino-6-hydroxypyrimidine sulphate (Hahn, *ibid.* 1917, 50, 705).

Nitrous acid or a nitrite may function as an oxidising agent, being reduced to  $NO$ ,  $H_2N_2O_2$ ,  $N_2O$ ,  $NH_2OH$ , nitrogen, or ammonia by stannous chloride, hydrogen sulphide, and sodium amalgam (Divers, *J.C.S.* 1899, 75, 87), by iodides:



and by electrolytic reduction (Tanatar, *Ber.* 1896, 29, 1039).

With hydrazine the following reaction is said to occur quantitatively and without evolution of nitrogen (Francke, *ibid.* 1905, 38, 4102; cf. Girard and Saporta, *Bull. Soc. chim.* 1904, [iii], 31, 905):



The molecular weight of nitrous acid in aqueous solution, found by the cryoscopic method, agrees with the formula  $HNO_2$  (Saposhnikov, *J. Russ. Phys. Chem. Soc.* 1909, 41, 1704). In most of its reactions the acid behaves as if it had the nitroso-constitution  $O=N-O-H$ ; the facts that many nitrites readily evolve  $NO_2$  on heating, and give nitroparaffins with alkyl iodides suggest the formula of a nitro-form



(Divers, *J.C.S.* 1885, 47, 226; Kieseritzky, *Z. physikal. Chem.* 1899, 28, 421; Baudisch, *Ber.* 1916, 49, 1176), but as more or less alkyl nitrite is formed in the second reaction it gives no definite clue to the constitution of nitrous acid. The reduction of nitrites to hyponitrites (p. 533a) supports the structure  $O=N-O-H$ , and there is some evidence that mercurous nitrite in solution is derived from this (Ley and Kissel, *Ber.* 1899, 32, 1357). Silver nitrite, on the other hand, is often regarded as derived from the nitro-form of the acid.

The nitrite ion has an angular form (Ziegler, *Physical Rev.* 1931, [ii], 38, 1040), similar to that

of the chlorite ion (Levi and Scherillo, *Z. Krist.* 1931, 76, 431).



#### HALIDES, ETC., OF NITROUS ACID.

Nitrosyl Fluoride, NOF, is prepared by the action of nitrosyl chloride on silver fluoride:  $\text{NOCl} + \text{AgF} = \text{NOF} + \text{AgCl}$ . A small flask containing nitrosyl chloride at  $-5^\circ$  is attached to one end of a long platinum tube containing the silver fluoride and kept at  $200-250^\circ$ , and the nitrosyl chloride slowly distilled. The product is condensed in a small platinum flask cooled in liquid air and on fractionation gives NOF as a colourless gas, b.p.  $-59.9^\circ$ , m.p.  $-132.5^\circ$ . In the cold, boron, silicon, red phosphorus, and arsenic take fire in the gas, sodium burns on heating, and antimony is at once acted on, the fluoride and nitric oxide being formed. Copper, aluminium, lead, and bismuth are slowly attacked, and tin reacts only on heating; iodine, sulphur, and carbon do not react even on heating. Moisture gives brown fumes, hydrofluoric and nitrous acid vapours being formed. Analysis and vapour density (1.701, air=1) agree with the formula NOF. The compound closely resembles nitryl fluoride,  $\text{NO}_2\text{F}$  (*q.v.*, p. 540c), in physical and chemical properties, but differs from it in its behaviour towards iodine and water. NOF gives additive compounds with  $\text{AsF}_5$  and  $\text{SbF}_5$  (Ruff *et al.*, *Z. anorg. Chem.* 1905, 47, 190; 1908, 58, 325; 1932, 208, 293).

Nitrosyl Chloride, NOCl, is obtained:

1. By the direct union of nitric oxide and chlorine:  $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$  (Gay-Lussac, *Ann. Chim. Phys.* 1848, [iii], 23, 203). The mixture of 2 vol. of NO and 1 vol. of chlorine is passed over dry finely granulated animal charcoal at  $40-50^\circ$  under slight pressure (Francesconi and Bresciani, *Atti R. Accad. Lincei*, 1903, [v], 12, ii, 75). The charcoal is not necessary and does not improve the yield (Briner and Pylkov, *J. Chim. phys.* 1912, 10, 640).

The formation of NOCl at low temperatures has been studied by Boubnoff and Guyo (*ibid.* 1911, 9, 290). After removing excess of NO at  $-160^\circ$  to  $-150^\circ$  an excess of chlorine (3-4%) above that required by the formula NOCl always remains, but is expelled at  $-80^\circ$ . According to Trautz (*Z. Elektrochem.* 1914, 20, 325; *J.C.S.* 1914, 106, ii, 457) the equation  $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$  does not satisfactorily explain the reaction at all temperatures investigated. Between  $-72^\circ$  and  $40^\circ$  the product is practically NOCl. At higher temperatures it is mixed with a gas richer in nitric oxide, perhaps  $(\text{NO})_2\text{Cl}$  or  $(\text{NO})_3\text{Cl}$ , and possibly with a gas richer in chlorine, perhaps  $\text{NOCl}_2$  (*cf.* Coates and Finnoy, *J.C.S.* 1914, 105, 2444; Wourtsel, *J. Chim. phys.* 1913, 11, 214).

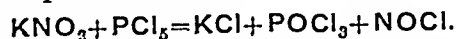
2. By heating *aqua regia*, a mixture of concentrated hydrochloric and nitric acids:



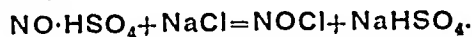
Nitrosyl chloride was first so obtained by Baudrimont (*Ann. Chim. Phys.* 1846, [iii], 17, 24; *cf.* Tilden, *J.C.S.* 1874, 27, 630; Goldschmidt,

Annalen, 1880, 205, 372) by liquefying it from the gas by cooling with ice and salt, but its composition was first determined by Gay-Lussac (*l.c.*). The reaction is reversible (Briner, *Compt. rend.* 1916, 162, 387).

3. By heating potassium nitrite with phosphorus pentachloride:



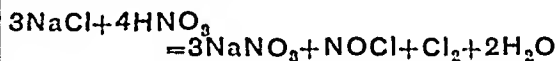
4. By heating nitrososulphuric acid (chamber crystals) with sodium chloride (Tilden, *l.c.*; Girard and Pabst, *Bull. Soc. chim.* 1878, [ii], 30, 531):



5. By the action of hydrogen chloride on  $\text{N}_2\text{O}_4$  (Müller, Annalen, 1862, 122, 1) and on  $\text{N}_2\text{O}_3$  (Briner and Wroczynski, *Compt. rend.* 1909, 149, 1372).

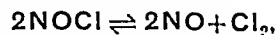
6. By the action of NO on  $\text{FeCl}_3$  heated to the sublimation point (Thomas, *ibid.* 1895, 120, 447).

7. Nitrosyl chloride, together with chlorine and some hydrogen chloride, is formed when sodium chlorido is evaporated with concentrated nitric acid:



(Gay-Lussac, *l.c.*), and it is obtained as a by-product in the production of sodium nitrate by this process (*see* p. 580c).

Nitrosyl chloride in an orange-yellow gas which condenses in a freezing mixture to a ruby-red mobile liquid, b.p.  $-5.6^\circ/761$  mm., giving lemon-yellow crystals, m.p.  $-61^\circ$  to  $-60^\circ$  (Francesconi and Bresciani, *l.c.*) or  $-61.5^\circ$  (Trautz and Gerwig, *Z. anorg. Chem.* 1924, 134, 409). The critical temperature is  $163-164^\circ$  (Francesconi and Bresciani, *l.c.*) or  $167^\circ$ , and the critical pressure 92.4 atm. (Briner and Pylkov, *J. Chim. phys.* 1912, 10, 640). The vapour density (2.29-2.32, air=1, at  $10^\circ$ ) is in agreement with the formula NOCl (Tilden, *l.c.*).  $\rho$  of liquid 1.4165 at  $-12^\circ$ ; 1.4250 at  $-15^\circ$ ; 1.4330 at  $-18^\circ$  (Geuther, Annalen, 1888, 245, 96; Briner and Pylkov, *l.c.*). The latent heat of evaporation is 5,560 g.-cal. per g.-mol. (Briner and Pylkov, *l.c.*). The gas is fairly stable towards heat, the dissociation:

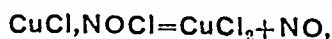


being first measurable at  $700^\circ$  (Sudborough and Miller, *J.C.S.* 1891, 59, 73, 270; Trautz *et al.*, *Z. anorg. Chem.* 1915, 93, 177; 1916, 97, 241) and the percentage dissociations are:

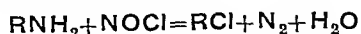
$784^\circ$	$816^\circ$	$968^\circ$	$985^\circ$
5.54	10.64	30.10	41.85

It has a characteristic absorption spectrum (Magnanini, *Z. physikal. Chem.* 1889, 4, 427).

With water, nitrosyl chloride hydrolyses to hydrochloric and nitrous acids, and it reacts with metals and metallic oxides to form the nitrite and chlorido (Sudborough, *J.C.S.* 1891, 59, 655). It forms compounds with many metallic chlorides, some of which decompose on heating with evolution of nitric oxide:



whilst others are stable and can be sublimed, e.g.,  $\text{AuCl}_3$ ,  $\text{NOCl}$  (Sudborough, l.c.; Gall and Mengdahl, Ber. 1927, 60 [B], 86; Rheinbold and Wasserfuhr, *ibid.*, p. 732), and with unsaturated organic compounds it forms additive compounds. With amines it evolves nitrogen and forms chlorides:



(Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431, 449, 606; for action on mercaptans, see Tasker and Jones, J.C.S. 1909, 95, 1910). Sulphur trioxide forms *nitrosyl sulphonic chloride*,  $\text{NO}\cdot\text{SO}_2\text{Cl}$ .

Nitrosyl chloride has been used in bleaching flour (B.P. 27218, 1908). It may be kept in vessels of magnesium alloys (Badische Anilin- u. Soda-Fabrik, G.P. 372575, 1921).

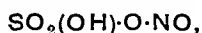
Nitrosyl Bromide,  $\text{NOBr}$ , is obtained as a dark brown liquid, m.p.  $-40^\circ$ , density 2.637 at  $20^\circ$ , (i) by the direct combination of NO and bromine at  $-7^\circ$  to  $-15^\circ$  (Landolt, Annalen, 1860, 116, 177); (ii) by the action of sodium bromide on nitrososulphuric acid (Girard and Pabst, Bull. Soc. chim. 1878, [iii], 30, 531; Trautz and Dalal, Z. anorg. Chem. 1920, 110, 1). It boils at  $-2^\circ$  with dissociation, thus differing from  $\text{NOCl}$ , which it resembles in its chemical properties.

Landolt's *dibromide*,  $\text{NOBr}_2$ , and Muir's *tribromide*,  $\text{NOBr}_3$ , are mixtures of the monobromide with bromine (Fröhlich, Annalen, 1884, 224, 270), but the melting-point diagram of bromine and nitric oxide (Trautz and Dalal, l.c.) shows a eutectic of bromine and *nitrosyl tribromide*, a maximum at  $-40^\circ$  corresponding with  $\text{NOBr}_3$ , and a second eutectic of  $\text{NOBr}_3$  and  $\text{NOBr}$  at above  $-55^\circ$ . Nitrosyl tribromide is a brownish-black, almost opaque liquid, which boils with decomposition at  $32^\circ$ ,  $d_4^{20}$  2.637. The corresponding iodine compound is unknown.

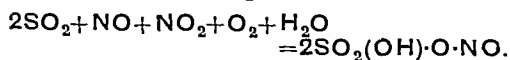
Nitrosyl Perchlorate,  $\text{NO}\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ , separates in colourless leaflets when " $\text{N}_2\text{O}_3$ " (i.e.  $\text{NO} + \text{NO}_2$ ) is passed into concentrated perchloric acid (b.p.  $140^\circ$ ). It forms addition compounds with unsaturated carbon compounds (Hofmann and Zedwitz, Ber. 1909, 42, 2031).

Nitrosyl Fluoborate,  $\text{NO}\cdot\text{BF}_4$ , is formed in colourless crystals on passing " $\text{N}_2\text{O}_3$ " into concentrated fluoboric acid,  $\text{HBF}_4$  (Wilke-Dörfurt and Balz, Z. anorg. Chem. 1927, 159, 197).

Nitrosyl Hydrogen Sulphate,  $\text{NO}\cdot\text{HSO}_4$ , also called *nitrososulphuric acid*,



*nitrosulphonic acid*,  $\text{NO}_2\cdot\text{SO}_3\text{H}$ , "chamber crystals," etc., was obtained by Clement and Desormes (Ann. Chim. Phys. 1806, [i], 59, 329; Davy, "Elements of Chemical Philosophy," 1812; "Works," 1840, Vol. IV, p. 204) by the action of nitrous fumes, oxygen, and a regulated amount of water on sulphur dioxide:



It is more conveniently obtained by passing a mixture of NO and  $\text{NO}_2$  into cooled concen-

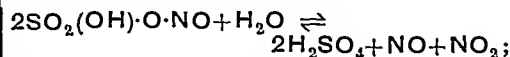
trated sulphuric acid (Weltzien, Annalen, 1860, 115, 213). but the best method of preparation (Weber, J. pr. Chem. 1862, [i], 85, 423; Ann. Phys. Chem. 1864, 123, 333; Berl *et al.*, Z. anorg. Chem. 1932, 209, 264) is to pass a slow stream of sulphur dioxide into well-cooled fuming nitric acid until a pasty mass is formed, and dry the crystals on a porous plate in a vacuum desiccator over concentrated sulphuric acid:



It is also formed by passing nitrosyl chloride into concentrated sulphuric acid (Tilden, J.C.S. 1874, 27, 630):



Nitrosyl hydrogen sulphate forms white prismatic crystals, melting with decomposition at  $73^\circ$  and forming the anhydride  $\text{O}(\text{NO}\cdot\text{O}\cdot\text{SO}_2)_2$  or  $\text{S}_2\text{N}_2\text{O}_9$ , which is obtained in other ways (*v. infra*). Nitrosyl hydrogen sulphate is violently decomposed by water:



it dissolves in concentrated sulphuric acid and in acid not containing more than 35% of water, but in more dilute acids it is decomposed (*cf.* Milligan and Gillette, J. Physical Chem. 1924, 28, 744). A corresponding *nitrosyl hydrogen selenate*,  $\text{NO}\cdot\text{HSeO}_4$ , is known (Hantzsch and Bergner, Z. anorg. Chem. 1930, 190, 321). There are no salts of nitrosyl hydrogen sulphate, and it is probably itself a salt  $[\text{NO}][\text{HSO}_4]$ , as is indicated by the Raman spectrum (Angus and Leckie, Trans. Faraday Soc. 1935, 31, 958), the deep-blue product of its reduction by metals or sulphur dioxide, formerly regarded by Raschig (J.S.C.I. 1911, 30, 166) as an acid  $\text{H}_2\text{SNO}_5$ , being  $[\text{NOH}][\text{HSO}_4]$ . This is the substance formulated by Sabatier (Compt. rend. 1896, 122, 1417, 1479, 1537; 1896, 123, 255) as  $\text{NO}(\text{SO}_3\text{H})_2$ .

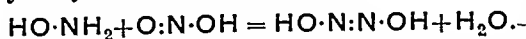
Dinitrososulphuric Anhydride, or Nitrosyl Disulphate,  $\text{S}_2\text{N}_2\text{O}_9$ , or  $\text{O}(\text{SO}_4\cdot\text{O}\cdot\text{NO})_2$ , or  $(\text{NO})_2\text{S}_2\text{O}_7$ , is formed as a white crystalline solid by passing dry nitric oxide into liquid sulphur trioxide and warming to the b.p.:  $3\text{SO}_3 + 2\text{NO} = \text{S}_2\text{N}_2\text{O}_9 + \text{SO}_2$ ; and by the action of sulphur dioxide on nitrogen peroxide in a sealed tube:  $2\text{SO}_2 + 3\text{NO}_2 = \text{S}_2\text{N}_2\text{O}_9 + \text{NO}$  (Weber, Ann. Phys. Chem. 1867, 130, 277; Hasenbach, J. pr. Chem. 1871, [ii], 4, 1; Friedburg, Chem. News, 1883, 47, 52; Briner, Lunge, and Van der Wijk, Helv. Chim. Acta, 1928, 11, 1125; Manchot and Schmid, Ber. 1929, 62 [B], 1261; Jones, Price, and Webb, J.C.S. 1929, 312). The compound  $\text{SO}_2(\text{O}\cdot\text{NO})_2$  could not be isolated.

#### HYPONITROUS ACID, ETC.

Hyponitrous Acid,  $\text{H}_2\text{N}_2\text{O}_2$ .—The existence of this acid was surmised by Maumené (Compt. rend. 1870, 70, 147); its sodium salt was first obtained by Divers (Proc. Roy. Soc. 1871, 19, 425) by reducing a solution of sodium nitrate with sodium amalgam. Divers (J.C.S. 1899, 75, 95) has given a nearly complete list of

various methods described for the production of hyponitrites, some of which give only traces or none at all.

1. By the interaction of nitrous acid and hydroxylamine in solution :



A nitrite and a hydroxylamino salt in aqueous solution (Wislicenus, Ber. 1893, 26, 771; Paal, *ibid.*, p. 1026), or free hydroxylamine and  $\text{N}_2\text{O}_3$  in methyl alcohol solution (Kaufmann, q. by Hantzsch and Sauer, Annalen, 1898, 299, 67, 98), may be used.

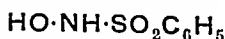
Sodium nitrite solution is added to a solution of hydroxylamine sulphate and the liquid rapidly heated to  $60^\circ$ , when nitrous oxide is briskly evolved. Silver nitrate solution is then added, when a canary-yellow precipitate of silver hyponitrite,  $\text{Ag}_2\text{N}_2\text{O}_2$ , should be formed; unless the silver nitrate is added at the right moment a dirty yellowish-white precipitate of silver nitrite is obtained.

2. The most satisfactory method of preparing a hyponitrite is by the reduction of a concentrated solution of sodium nitrite with sodium amalgam (25 g. of sodium in 140 c.c. of mercury), the flask being cooled with running water (Divers, J.C.S. 1899, 75, 95; modified by Partington and Shah, *ibid.* 1931, 2071; 1932, 2589). The hyponitrite is most stable in presence of excess of alkali. After the reduction any hydroxylamine formed may be removed by adding mercuric oxide and, after neutralisation with nitric acid, silver nitrate solution is added to the liquid, when  $\text{Ag}_2\text{N}_2\text{O}_2$  is precipitated; it is more convenient, however, to use excess of sodium amalgam, when the hydroxylamine is reduced to ammonia, which is eliminated by evaporation in a vacuum desiccator over concentrated sulphuric acid, when crystals of  $\text{Na}_2\text{N}_2\text{O}_2$  with 5 or  $8\text{H}_2\text{O}$  separate. These are crushed, triturated with absolute alcohol, washed with absolute alcohol and ether, and dried in a desiccator over concentrated sulphuric acid, when a stable white powder of anhydrous  $\text{Na}_2\text{N}_2\text{O}_2$  ( $p^{25}$  1.726) is obtained. Magnesium amalgam can also be used (Noogi and Nandi, *ibid.* 1928, 1449).

3. By passing nitric oxide into a solution of sodium in liquid ammonia (Joannis, Compt. rend. 1894, 118, 715), but Zintl and Hardor (Ber. 1933, 66 [B], 760) say the product is not a true hyponitrite. The action of nitric oxide on the sodium compound of pyridine (Weitz and Vollmer, *ibid.* 1924, 57 [B], 1015) has been recommended, but the product is contaminated by impurities.

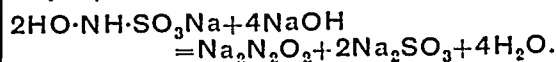
4. By oxidising hydroxylamine with metallic oxides ( $\text{CuO}$ ,  $\text{HgO}$ ,  $\text{Ag}_2\text{O}$ ) (Hantzsch and Kauffmann, Annalen, 1892, 292, 317), or sodium hypobromite (Kolotow, J. Russ. Phys. Chem. Soc. 1900, 23, 3; Bull. Soc. chim. 1891, [iii], 6, 924).

5. By the alkaline hydrolysis of hydroxylamine monosulphonic acid,  $\text{HO}\cdot\text{NH}\cdot\text{SO}_3\text{H}$  (Divers and Haga, J.C.S. 1899, 75, 77) or  $\beta$ -benzene sulphonyl hydroxylamino,



(Piloty, Ber. 1896, 29, 1559).

6. By treating sodium hydroxylamine monosulphonate (v. HYDROXYLAMINE, Vol. VI, 403b) with concentrated or fused alkali; a 60% yield of  $\text{Ag}_2\text{N}_2\text{O}_2$  is said to be obtained by precipitation (Kirschner, Z. anorg. Chem. 1892, 16, 424; Hantzsch and Sauer, Annalen, 1898, 299, 67; Wieland, *ibid.* 1903, 329, 225):



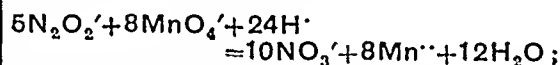
Divers reports a poor yield by this method, and states that reduction of nitrites by aluminium amalgam, ferrous hydroxide, or fusion with iron filings, is useless.

Free hyponitrous acid is obtained by treating the silver salt with a solution of hydrogen chloride in dry ether, and evaporating the filtrate in a desiccator. White crystalline leaflets are obtained which almost at once decompose spontaneously with slight explosion, or otherwise by friction or contact with solid potassium hydroxide or acid vapours (Hantzsch and Kaufmann, *l.c.*; Partington and Shah, *l.c.*). The crystals are too unstable to allow of analysis, but the molecular weight from the freezing-point of the aqueous solution corresponds with the formula  $\text{H}_2\text{N}_2\text{O}_2$ . The crystals are readily soluble in water and alcohol and are fairly soluble in most organic solvents. The acid decomposes irreversibly:  $\text{H}_2\text{N}_2\text{O}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$ ; small amounts of nitric and nitrous acids are also formed (Rây and Ganguli, J.C.S. 1907, 91, 1866). The heat of formation is

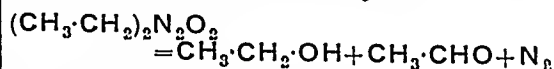


(Berthelot, Ann. Chim. Phys. 1880, [vi], 18, 571).

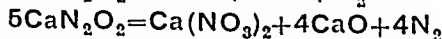
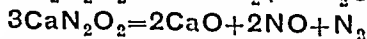
Hyponitrous acid and its salts are oxidised to nitric acid by bromine and by acid permanganate:



sodium amalgam does not reduce them, but the free acid is reduced to hydrazine by  $\text{NaHSO}_3$  (Brackel, Ber. 1900, 33, 2115). The acid forms normal salts  $\text{M}_2\text{N}_2\text{O}_2$  and some acid salts  $\text{M}^+\text{HN}_2\text{O}_2$ , the latter being very unstable although  $\text{Ba}(\text{HN}_2\text{O}_2)_2$  and  $\text{NH}_4\text{HN}_2\text{O}_2$  have been obtained. The normal salts are mostly obtained by precipitation (Divers, *l.c.*; Noogi and Nandi, *l.c.*; Partington and Shah, *l.c.*). Esters are formed by the action of the iodides on silver hyponitrite. The ethyl ester is a yellow oil (Zorn, Ber. 1878, 11, 1630), the benzyl ester a solid (Hantzsch and Kauffmann, *l.c.*; for other esters, see Partington and Shah, *l.c.*). The molecular weights of the esters in solution corresponds with  $\text{R}_2\text{N}_2\text{O}_2$ . On heating they decompose with evolution of nitrogen and the formation of an alcohol and an aldehyde:

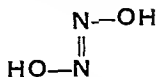


The salts decompose on heating:



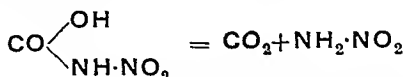
(Partington and Shah, J.C.S. 1932, 2589).

The formula of hyponitrous acid as the *anti*-form of diazodihydroxide:

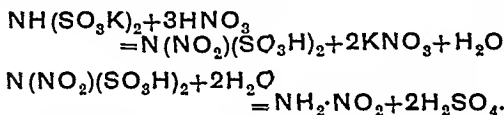


proposed by Hantzsch, is confirmed by the very small dipole moments of its esters (Hunter and Partington, *ibid.* 1933, 309).

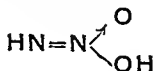
Nitramide,  $\text{NH}_2 \cdot \text{NO}_2$ , is isomeric with hyponitrous acid but is somewhat more stable, forming white crystals, m.p.  $72^\circ$  with decomposition:  $\text{NH}_2 \cdot \text{NO}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$ . It is formed by the action of excess of cold concentrated sulphuric acid on potassium nitrocarbamate (Thiele and Lachmann, Ber. 1894, 27, 1909; Annalen, 1895, 288, 267; Brønsted and Pedersen, Z. physikal. Chem. 1924, 108, 185; Marlies and La Mer, J. Amer. Chem. Soc. 1935, 57, 2008; Hunter and Partington, *l.c.*):



or (in poor yield) by nitrating potassium imido-disulphonate in concentrated sulphuric acid and pouring on ice:

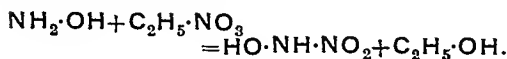


Although Hantzsch suggested that nitramide is the *syn*-isomer of hyponitrous acid (Annalen, 1896, 292, 340; 1897, 296, 111) he later abandoned this improbable theory (Ber. 1930, 63 [B], 1270). Thiele and Lachmann (Annalen, 1897, 296, 100) prefer the formula  $\text{NH}_2 \cdot \text{NO}_2$ , which is generally accepted, but admit the possibility that the substance is the imide of nitric acid,

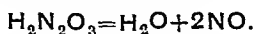


It forms a mercuric salt,  $\text{HgN} \cdot \text{NO}_2$ , and hence has some acidic function.

Hyponitric Acid,  $\text{H}_2\text{N}_2\text{O}_3$  (usually called *nitrohydroxylamic acid*), is formed as the sodium salt by the action of ethyl nitrate on a solution of free hydroxylamine in methyl alcohol in presence of sodium methoxide (Angeli, Gazzetta, 1896, 26, ii, 17; "Sammlung chem.- und chem.-techn. Vorträge," ed. by Ahrens and Herz, 1908, 13; Malachta, Coll. Czech. Chem. Comm. 1938, 10, 32):



The sodium salt  $\text{Na}_3\text{N}_2\text{O}_3$ , which forms a hydrate with  $1\text{H}_2\text{O}$ , is fairly stable, but on acidification the free acid instantly decomposes with evolution of nitric oxide:



The existence of  $\text{H}_2\text{N}_2\text{O}_3$  as an intermediate stage in the oxidation of  $\text{NH}_2\text{OH}$  by permanganate was suggested by Thum (Monatsh. 1893, 14, 303).

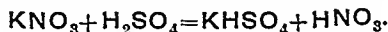
Hydronitrous Acid,  $\text{H}_2\text{NO}_2$ , is known as a deep yellow sodium salt,  $\text{Na}_2\text{NO}_2$ , exploding in contact with moist air, obtained by the action of sodium on sodium nitrite in liquid ammonia (Maxted, J.C.S. 1917, 111, 1016; Zintl and Kohn, Ber. 1928, 61 [B], 189).

#### NITRIC ACID.

Nitric acid,  $\text{HNO}_3$ , is, after ammonia, the oldest known nitrogen compound. It has been supposed that the ancient Egyptians used it to dissolve silver (J. R. Partington, "Origins and Development of Applied Chemistry," Longmans, 1935, p. 149). It is described in the Latin works ascribed to Geber, which were probably written about 1150, and in the "Pro Conservanda Sanitate" (Maintz, 1531) of Vital du Four (died 1327), compiled from older sources, in which its preparation by distilling saltpetre (*sal petræ*) with green vitriol (*corrossa*) is mentioned. It was well known to the alchemists from the fourteenth century (H. Kopp, "Geschichte der Chemie," 1845, Vol. III, p. 219; Guttmann, J.S.C.I. 1901, 20, 5), who obtained it by several wasteful processes, most of which feature in recent patent specifications, and called it *aqua dissolutiva*, *aqua acutis*, or *aqua fortis*. It was used in the sixteenth century for parting gold and silver, and hence was called *chrysulca* or "eau de départ" (Budé, 1516). The concentrated fuming acid (called *spiritus nitri acidus*, *spiritus nitri fumons* Glauber, etc.) was prepared by Glauber about 1658 by the satisfactory method of distilling saltpetre (nitre,  $\text{KNO}_3$ ) with concentrated sulphuric acid. The composition of nitric acid was investigated by Lavoisier in 1776 ("Oeuvres," Vol. II, p. 129), who found that it could be formed by the oxidation of nitric oxide, but it was Cavendish in 1785 (Phil. Trans. 1785, 75, 372) who first showed that it contained oxygen and nitrogen, since potassium nitrate was found by sparking a mixture of these two gases in contact with potash solution. The quantitative composition was established by Gay-Lussac (Ann. Chim. Phys. 1816, [ii], 1, 394; T. M. Lowry, "Historical Introduction to Chemistry," Macmillan, 1915, p. 197).

Nitric acid is formed by electrical discharges in the atmosphere, and by the oxidation of nitrogenous organic matter by bacteria in the soil in the presence of bases (p. 544a), and it occurs as Bengal saltpetre ( $\text{KNO}_3$ ) and Chile saltpetre ( $\text{NaNO}_3$ ). It is formed by the action of suitable oxidising agents on ammonia (r. NITROGEN, ATMOSPHERIC, UTILISATION OF, this Vol., p. 544a), and on less oxidised compounds of nitrogen, and by electrolytic and biochemical oxidation.

On the small scale, nitric acid is made by distilling equimolecular amounts of potassium or sodium nitrate with concentrated sulphuric acid in a stoppered retort:



Ammonium nitrate reacts peculiarly with concentrated sulphuric acid (Pelouze, Ann. Chim. Phys. 1841, [ii], 2, 47); when the dry nitrate is heated with excess of concentrated sulphuric acid at  $90-120^\circ$  nitric acid distills, but at  $150^\circ$

the sole products are nitrous oxide and water, no nitric acid being formed.

When the distillation of the sodium or potassium nitrate with sulphuric acid is carried out in a stream of carbon dioxide a 98% acid can be obtained. Fractional crystallisation of the acid gives a  $99.4 \pm 0.1\%$  acid. Absolute nitric acid exists only in the form of snow-white crystals, m.p.  $-41^\circ$  (Biltz and Hülsmann, *Z. anorg. Chem.* 1932, 207, 377) or  $-41.5^\circ$  (Briner, Susz, and Favarger, *Helv. Chim. Acta*, 1935, 18, 375). On melting these, a yellow liquid results, which is a solution of a little nitrogen pentoxide and water in nitric acid:  $2\text{HNO}_3 \rightleftharpoons \text{N}_2\text{O}_5 + \text{H}_2\text{O}$  (Küster and Munch, *Z. anorg. Chem.* 1905, 43, 350).

The most concentrated liquid acid is prepared by repeatedly distilling ordinary pure concentrated nitric acid with its own (or twice) its volume of concentrated sulphuric acid in an all-glass vacuum apparatus protected from light (Veley and Manley, *Phil. Trans.* 1898, 191, 365; cf. L. Meyer, *Ber.* 1889, 22, 23; Mischtschenko, *J. Appl. Chem. Russia*, 1929, 2, 521; Lühdemann, *Z. physikal. Chem.* 1935, 29, 133).

The freezing-point diagram (Fig. 7) shows two

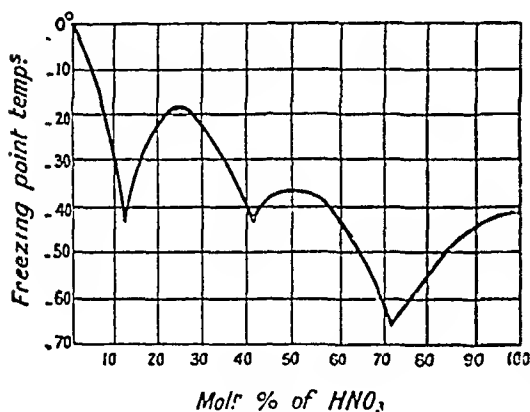


FIG. 7.

maxima corresponding with the crystal hydrates,  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  ( $-38^\circ$ ) and  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  ( $-18.5^\circ$ ), and three minima corresponding with the eutectic mixtures (1) ice +  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  ( $-43^\circ$ ), (2)  $\text{HNO}_3 \cdot 3\text{H}_2\text{O} + \text{HNO}_3 \cdot \text{H}_2\text{O}$  ( $-42^\circ$ ), and (3)  $\text{HNO}_3 \cdot \text{H}_2\text{O} + \text{HNO}_3$  ( $-66^\circ$ ) (Pickering, *J.C.S.* 1893, 63, 436; Küster and Kromann, *Z. anorg. Chem.* 1904, 41, 1). The existence of solid hydrates of nitric acid was recognised by Cavendish from experiments by McNab at Hudson Bay (*Phil. Trans.* 1786, 76, 241; 1788, 78, 166). Other solid hydrates, formulated as  $\text{N}(\text{OH})_5$ ,  $\text{O}[\text{N}(\text{OH})_2]_2$  and  $\text{O}[\text{NO}(\text{OH})_2]_2$  (Erdmann, *Z. anorg. Chem.* 1902, 32, 431; *Z. angew. Chem.* 1903, 16, 1001), are not shown on the freezing-point diagram; the existence of  $\text{N}(\text{OH})_5$  in solution has been inferred from the refractive indices (Veley and Manley, *Proc. Roy. Soc.* 1901, 68, 128; 1901, 69, 86; *J.C.S.* 1903, 83, 1015) and absorption spectra (Hartley, *Proc. Roy. Dublin Soc.* 1905, [ii], 10, 373), but the evidence is insufficient (Küster and Kromann, *l.c.*; Küster, *Z. angew. Chem.* 1903, 16, 1079). The hydrate  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  might be formulated  $\text{H}_3\text{NO}_4$  or  $\text{O} \leftarrow \text{N}(\text{OH})_3$ , analogous

to orthophosphoric acid. The Raman spectra (Dadiou and Kohlrausch, *Naturwiss.* 1931, 19, 690) indicate that aqueous solutions of nitric acid contain a considerable amount of the pseudo-form  $\text{HO} \cdot \text{NO}_2$ , and the pure acid is exclusively this, the ionic form  $\text{H}^+ \text{NO}_3^-$  being progressively formed on dilution. No evidence of the presence of the nitronium nitrate form  $[\text{NO}(\text{OH})_2]\text{NO}_3$ , postulated by Hantzsch and Berger (*Ber.* 1928, 61 [B], 1328), was found, the  $\text{NO}_3^-$  frequency being absent.

The density of "100%" nitric acid ( $\rho_4^{20}$ ) is 1.503 (Briner, Susz, and Favarger, *Helv. Chim. Acta*, 1935, 18, 375) and of 99.97% acid ( $\rho_4^{23}$ ) 1.50269 (Lühdemann, *Z. physikal. Chem.* 1935, B, 29, 133). The densities of solutions of different concentrations at different temperatures have been determined by several investigators (Lunge and Rey, *Z. angew. Chem.* 1891, 165; Veley and Manley, *l.c.*, and *J.S.C.I.* 1903, 22, 1227; Bousfield, *J.C.S.* 1915, 107, 1405).

The following table is constructed from Lunge and Rey's values:

$\rho_4^{15}$	$\text{HNO}_3$ , %	$\rho_4^{15}$	$\text{HNO}_3$ , %
1.00	0.10	1.30	47.49
1.05	8.99	1.35	55.70
1.10	17.11	1.40	65.30
1.15	24.84	1.45	77.23
1.20	32.36	1.50	94.09
1.25	39.82	1.52	99.07

The density of  $\text{n-HNO}_3$  (63.13 g. per l.) at  $18^\circ$  is 1.0324 (Loomis, *Ann. Phys. Chem.* 1897, [iii], 60, 523) and at  $18.6^\circ$  1.0318 (Kohlrausch, *ibid.* 1885, [iii], 26, 161). Bousfield (*l.c.*) gives for  $18^\circ$ :

N.	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$
$\rho_4^{18}$	1.0324	1.0150	1.0072	1.00293	1.00080	0.99973

The density of concentrated nitric acid containing  $\text{N}_2\text{O}_4$  ("fuming nitric acid") increases with the weight percentage of  $\text{N}_2\text{O}_4$  to 42.5%, when it reaches a maximum; this corresponds with the composition  $\text{HNO}_3 \cdot \text{NO}_2$ , and the reciprocal solubility of nitric acid and nitrogen peroxide at different temperatures is said (Pascal and Garnier, *Bull. Soc. chim.* 1919, [iv], 25, 309; cf. Bousfield, *J.C.S.* 1919, 115, 45; Lowry, Lloyd, and Lloyd, *ibid.* 1936, 10) to indicate that this is a definite compound stable below  $-48.5^\circ$  but dissociating above this temperature with liberation of  $\text{N}_2\text{O}_4$ .

The thermal expansion of dilute (Forch, *Ann. Phys. Chem.* 1895, [iii], 55, 100; Ostwald, *J. pr. Chem.* 1877, [ii], 16, 385) and concentrated (Küster and Kromann, *l.c.*) solutions has been studied; in concentrated solutions the expansion-concentration curve shows two breaks at 54.0%  $\text{HNO}_3$  ( $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ) and 77.77%  $\text{HNO}_3$  ( $\text{HNO}_3 \cdot \text{H}_2\text{O}$ ), corresponding with the compositions of the solid hydrates.

The viscosity of "100%" nitric acid at  $24.9^\circ$  is  $\eta = 0.0076$  poise. The viscosities of aqueous solutions (Graham, *Phil. Trans.* 1861, 151, 373; *J.C.S.* 1862, 15, 427; Paggliani and Oddone, *Atti Accad. Torino*, 1887, 22, 314;



Reyher, Z. physikal. Chem. 1888, 2, 744; Küster and Kremann, Z. anorg. Chem. 1904, 41, 1; Bousfield, J.C.S. 1915, 107, 1781; Bingham and Stone, J. Physical Chem. 1923, 27, 701; Rhodes and Hodge, Ind. Eng. Chem. 1929, 21, 142) of various concentrations at various temperatures have been determined. Bingham and Stone found (in centipoises):

Wt. %	12.65	25.28	38.05	52.18	62.66
10°	1.329	1.500	1.842	2.390	2.647
20°	1.057	1.210	1.509	1.883	—
40°	0.724	0.848	1.033	1.286	1.369
Wt. %	69.86	77.24	88.34	99.19	
10°	2.609	2.487	1.790	1.070	
20°	2.039	1.952	1.452	0.913	
40°	1.356	1.312	1.025	0.698	

Bousfield, for solutions of normality  $N$ , found (in centipoises;  $\eta$  for water at 18° = 1.0514 centipoise):

$N$	4°	11°	18°	25°
1	1.5487	1.2807	1.0731	0.9176
$\frac{1}{2}$	1.5513	1.2684	1.0590	0.9011
$\frac{1}{3}$	1.5552	1.2655	1.0546	0.8969
$\frac{1}{4}$	1.5586	1.2651	1.0519	0.8943
$\frac{1}{5}$	1.5605	1.2663	1.0525	0.8927
$\frac{1}{6}$	1.5630	1.2672	1.0528	0.8920

There is a maximum viscosity at about 65%  $\text{HNO}_3$ .

The surface tension,  $\gamma$ , in dynes per cm. of pure nitric acid is: 11.6° 41.30, 46.2° 35.95, 78.2° 31.46 (Aston and Ramsay, J.C.S. 1894, 65, 167), and those of solutions at 20° (Jahnke, Dissert. Heidelberg, 1909, quoted in Beibl. Ann. Physik, 1910, 34, 519):

Wt. % $\text{HNO}_3$	7.35	9	22	37	50	70
$\gamma$	73.10	72.70	71.48	68.10	65.43	59.36

The boiling-point of the purest nitric acid is 86° with decomposition, or 21.5° at 24 mm. (Erdmann, Z. anorg. Chem. 1902, 32, 431; Berl and Samtleben, Z. angew. Chem. 1922, 35, 201). The solution in water has a maximum boiling-point: 120.5° at 735 mm. (68.0%  $\text{HNO}_3$ ); at 1,220 mm. the azeotropic solution contains 68.6% of  $\text{HNO}_3$  (Roscoe, Annalen, 1860, 116, 203; J.C.S. 1861, 13, 146). Although the azeotropic solution at 1 atm. pressure (first investigated by Dalton) corresponds approximately with  $2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , it is not a definite compound. By passing an indifferent gas through the acid at ordinary temperature residues differing widely in composition are obtained.

The vapour pressures of nitric acid solutions and the boiling-points under various total pressures have often been investigated (Saposhnikoff, Z. physikal. Chem. 1905, 53, 225; Creighton and Githens, J. Franklin Inst. 1915, 179, 161; Creighton and Smith, *ibid.* 1915, 180, 703; Sproesser and Taylor, J. Amer. Chem. Soc. 1921, 43, 1782; Taylor, Ind. Eng. Chem. 1925, 17, 633; Perry and Davis, Chem. Met. Eng. 1934, 41, 188; Wilson and Miles, Trans. Faraday Soc. 1940, 36, 356; Forsythe and Giauque, J. Amer. Chem. Soc. 1942, 64, 48, 3069; 1943, 65, 2479).

The following table is compiled from Taylor's figures.  $A$  is the partial pressure in millimetres of  $\text{HNO}_3$  and  $B$  the partial pressure in millimetres of  $\text{H}_2\text{O}$  in the vapour in equilibrium with liquid acid of weight-%  $\text{HNO}_3$  shown on the left. The sum of  $A$  and  $B$  gives the total vapour pressure. A hyphen shows that the partial vapour pressure is inappreciable; blank spaces indicate that no values were determined.

% $\text{HNO}_3$	0°.	15°.	25°.	40°.	60°.	80°.	100°.	115°.	125°C.
20 $A$	-	-	-	-	-	0.53	1.87		
$B$	4.1	10.9	20.6	47.5	128	307	675		
30 $A$	-	-	-	0.11	0.51	1.87	6.05		
$B$	3.6	9.7	17.8	41	113	267	580		
40 $A$	-	-	0.12	0.36	1.48	5.1	15.5	32.5	
$B$	3	8	14.6	33.5	90	218	480	810	
60 $A$	0.19	0.59	1.21	3.10	9.9	27.5	69.5	126	187
$B$	1.5	4.1	7.7	18.1	51	126	285	495	700
70 $A$	0.79	2.18	4.10	9.65	27.1	67.5	152	262	372
$B$	1.1	3	5.5	12.8	35.3	86	192	330	469
80 $A$	2	6	10.5	24.5	67	158	330	545	
$B$	-	1.7	3.2	7	20	45	108	185	
90 $A$	5.5	15	27	62	157	338	675		
$B$	-	-	1	2.4	6.5	16	35		
100 $A$	11	30	57	133	320	625			

In mixtures of concentrated nitric and sulphuric acids the vapour pressure rises to a maximum and then falls with increasing percentage of  $\text{HNO}_3$ . With  $\text{HNO}_3$  of  $\rho$  1.40 the maximum (23.5 mm.) is with 45% of  $\text{HNO}_3$ , and with  $\text{HNO}_3$  of  $\rho$  1.48 the maximum (34 mm.) is with 67% of  $\text{HNO}_3$ . With the pure acids the value rises steadily to 41 mm. with 80% of  $\text{HNO}_3$ , remains constant up to 92% of  $\text{HNO}_3$ , and then rises to 46 mm. with pure  $\text{HNO}_3$ . These values are at 15° (Saposhnikoff, Z. physikal. Chem. 1904, 49, 697; 1905, 51, 609; 1905, 53, 225). Pascal (Compt. rend. 1917,

165, 589; Pascal and Garnier, Ann. Chim. 1921, [ix], 15, 253; P. Pascal, "Traité de Chimie minérale," Masson, Paris, 1932, 3, 242) has studied the vapour pressures of the system  $\text{SO}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$  and represented them on a triangular diagram.

The specific heats of solid and liquid  $\text{HNO}_3$  and the two hydrates (Forsythe and Giauque, J. Amer. Chem. Soc. 1942, 64, 48; 1943, 65, 2479) at various temperatures (g.-cal. per g.-mol.) are shown in the Table below; the melting-points are:  $\text{HNO}_3$  231.51° K.,  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  235.48° K.,  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  254.63° K., and



above these temperatures the substances are liquid:

$T, ^\circ\text{K.}$	20	40	80	100	150
$\text{HNO}_3$	1.238	4.468	8.825	10.06	12.37
$\text{HNO}_3 \cdot \text{H}_2\text{O}$	1.228	4.708	10.37	12.34	15.87
$\text{HNO}_3 \cdot 3\text{H}_2\text{O}$	2.009	7.826	17.06	20.37	27.12

$T, ^\circ\text{K.}$	200	250	270	300
$\text{HNO}_3$	14.70	26.65	26.51	26.24
$\text{HNO}_3 \cdot \text{H}_2\text{O}$	18.77	43.19	43.41	43.62
$\text{HNO}_3 \cdot 3\text{H}_2\text{O}$	33.22	40.61	75.94	77.80

The latent heat of fusion of  $\text{HNO}_3$  is 2,503 g.-cal. per g.-mol., of  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  4,184 g.-cal. per g.-mol., and of  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  6,954 g.-cal. per g.-mol. (Forsythe and Giauque, *l.c.*). The latent heat of evaporation of  $\text{HNO}_3$  is approximately 7,250 g.-cal. per g.-mol. at the boiling-point (Berthelot, *Ann. Chim. Phys.* 1877, [v], 12, 529), or about 9,355 g.-cal. per g.-mol. at  $25^\circ\text{C}$ . (Wilson and Miles, *Trans. Faraday Soc.* 1940, 36, 356). The entropy of liquid  $\text{HNO}_3$  at  $25^\circ\text{C}$ . is 37.19 g.-cal. per g.-mol. per degree, and of the gas 63.6 g.-cal. per g.-mol. per degree at  $25^\circ\text{C}$ . and 1 atm. (Forsythe and Giauque, *l.c.*).

The specific heats of nitric acid solutions, with  $n$  mol. of  $\text{HNO}_3$  to 1 mol. of  $\text{H}_2\text{O}$ , at  $20^\circ$  (Pascal and Garnier, *Bull. Soc. chim.* 1920, [iv], 27, 8) are:

$n$	10.0	25.57	40	60.52
G.-cal. per g.	0.900	0.787	0.699	0.637

$n$	81.80	92.15	98.15
G.-cal. per g.	0.575	0.500	0.475

The specific heats  $c$  g.-cal. per g. of more dilute solutions were measured by Marignac at  $21$ – $52^\circ$  (*Ann. Chim. Phys.* 1876, [v], 8, 410) and J. Thomsen at  $18^\circ$  ("Thermochemische Untersuchungen," Leipzig, 1882, Vol. I, p. 38):

$n$	5	10	12.5	20
$c$	0.7212 <sup>2</sup>	0.768 <sup>1</sup>	0.8043 <sup>2</sup>	0.849 <sup>1</sup>

$n$	25	50	100	200
$c$	0.8752 <sup>2</sup>	0.930 <sup>1</sup>	0.963 <sup>1</sup>	0.982 <sup>1</sup>
		0.9273 <sup>2</sup>	0.9618 <sup>2</sup>	

$n$ =no. of mol. of  $\text{H}_2\text{O}$  per mol. of  $\text{HNO}_3$ ; <sup>1</sup> Thomsen, <sup>2</sup> Marignac.

The heat of dilution (g.-cal. evolved) for 1 g.-mol. of  $\text{HNO}_3$  in  $n$  g.-mol. of water is given by the formula  $8,974n/(n+1.737)$  (J. Thomsen, "Thermochemische Untersuchungen," Leipzig, 1883, Vol. III, p. 34; cf. Richards and Rowe, *J. Amer. Chem. Soc.* 1921, 43, 779; Rossini, *J. Res. Nat. Bur. Stand.* 1931, 6, 791; 1931, 7, 47; Forsythe and Giauque, *l.c.*, who calculate 7,971 g.-cal. per g.-mol. to infinite dilution from their experiments).

The heat of formation (evolved) of nitric acid in aqueous solution  $\text{H} + \text{N} + 3\text{O} + \text{Aq.} = \text{HNO}_3 \cdot \text{Aq.}$  is 49,090 g.-cal. (Thomsen, *op. cit.*, 1882, Vol. II, p. 199;  $\text{Aq.} = 300\text{H}_2\text{O}$ ) or 48,800 g.-cal. (Berthelot, "Thermochemie," Gauthier-Villars, 1897, Vol. II, p. 107) from which, by subtracting the heat of solution, 7,480 g.-cal. (Thomsen) or 7,180 g.-cal. (Berthelot), the heat of formation of the pure liquid acid  $\text{H} + \text{N} + 3\text{O} = \text{HNO}_3$ , is found to be 41,610 g.-cal. (Thomsen) or 41,620 g.-cal. (Berthelot). From the data of Roth and Becker (*Z. Elektrochem.* 1934, 40, 836), Forsythe and Giauque (*l.c.*) calculate 41,349 g.-cal., and for the available energy ( $G = E - TS + PV$ ) change at  $25^\circ\text{C}$ .  $\Delta G = -11,539$  g.-cal.

The refractive indices of concentrated nitric acid at  $20^\circ$  (Brühl, *Z. physikal. Chem.* 1897, 22, 373) are:

$D_{20}^{20}$	$D$	$H_\alpha$	$H_\beta$	$H_\gamma$
1.50999	1.39584	1.39309	1.40267	1.40374
1.50375	1.39637	1.39407	1.40363	1.40398

The refractive indices of solutions show a maximum value (1.4061 at  $14.2^\circ$  for  $D$  line) for 70%  $\text{HNO}_3$ , the values for 50% and 99% acids being practically identical (Voley and Manley, *Proc. Roy. Soc.* 1901, 68, 128; 1901, 69, 86). Nitric acid of concentration above 65% is decomposed by light and becomes yellow:



(Berthelot, *Compt. rend.* 1898, 127, 143; Voley and Manley, *Phil. Trans.* 1898, 191, 365). Only the vapour is decomposed, the liquid acid in a completely filled bottle remaining colourless. The reaction is reversible, the products of decomposition recombining in the dark. The anhydrous (100%) acid decomposes in the dark (Reynolds and Taylor, *J.C.S.* 1912, 101, 131).

The mass magnetic susceptibility of nitric acid is  $\chi = -0.306 \times 10^{-6}$  c.g.s. units (Schaffer and Taylor, *J. Amer. Chem. Soc.* 1926, 48, 843).

The electrical conductivity,  $\kappa$ , in  $\text{ohm}^{-1} \text{cm}^{-1}$  of nitric acid solutions of concentrations  $c$  g.-mol. per l. at  $25^\circ$  is (D. F. Smith, *ibid.* 1923, 45, 362; cf. Kohlrausch, *Ann. Phys. Chem.* 1885, 26, 161; Arrhenius, *Z. physikal. Chem.* 1889, 4, 96; Loomis, *Ann. Phys. Chem.* 1897, 60, 547; Voley and Manley, *Proc. Roy. Soc.* 1897, 62, 223; Küster and Kremann, *Z. anorg. Chem.* 1904, 41, 1):

$c$	0.3007	0.5105	1.0105	2.5110	3.3452
$\kappa$	0.1112	0.1850	0.3335	0.0514	0.7585

Voley and Manley found two irregularities in the conductivity-concentration curve at 25 and 50 mol.-%  $\text{HNO}_3$ , corresponding with the hydrates  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ , and a third at 96–100 mol.-%, perhaps corresponding with the formation of  $\text{N}_2\text{O}_5$ . Nitrates increase the conductivity of concentrated nitric acid in proportion to the amount dissolved (Bouty, *Compt. rend.* 1888, 106, 595, 654). The equivalent conductivity  $\Lambda = \kappa v$   $\text{ohm}^{-1} \text{cm}^2$  at  $25^\circ$  ( $v$ =dilution in l. per g.-equiv.) is (Hlasko and Klimowski, *Bull. Acad. Polonaise* 1932, A, 257; cf. Kohlrausch and Grotrian, *Ann. Phys. Chem.* 1875, 154, 1, 215; Noyes *et al.*, *Z. physikal. Chem.* 1910, 70, 335):

$v$	2	8	32	128	512	2,048	$\infty$
$\Lambda$	347.2	390.7	397.9	408.2	414.8	418.9	425.9

The temperature coefficient of  $\Lambda$  is 0.015 at  $18$ – $100^\circ$  (Arrhenius, *l.c.*).

The transport number of  $\text{NO}_3^-$  in 0.1N- $\text{HNO}_3$  at  $25^\circ$  is 0.1559 (MacInnes and Cowperthwaite, *Trans. Faraday Soc.* 1927, 23, 400) and the mobility of  $\text{NO}_3^-$  at infinite dilution at  $25^\circ$  is  $71.42 \text{ ohm}^{-1} \text{cm}^2$  (MacInnes, Shedlovsky, and Longworth, *J. Amer. Chem. Soc.* 1932, 54, 2578; Stonehill, *J.C.S.* 1943, 647).

The freezing-points of nitric acid solutions (Jones, *Z. physikal. Chem.* 1893, 12, 623; Jones and Getman, *Amer. Chem. J.* 1902, 27, 433; Noyes and Falk, *J. Amer. Chem. Soc.* 1910, 32,

1011; Abel, Redlich, and von Lengyel, Z. physikal. Chem. 1923, 132, 189) and the corresponding calculated activity coefficients,  $\gamma$ , at the freezing-point are:

$m$	0.005	0.01	0.05	0.1	0.5
$\theta/m$	3.63	3.60	3.516	3.494	3.498
$\gamma$	0.930	0.905	0.827	0.784	0.708

$m$	1.0	2.0	3.0	4.0	
$\theta/m$	3.605	3.861	4.143	4.442	
$\gamma$	0.706	0.759	0.845	0.959	

( $m$ =molality (g.-mol. of  $\text{HNO}_3$  per 1,000 g. of  $\text{H}_2\text{O}$ ),  $\theta$ =freezing-point depression,  $\theta/m$ =molal depression.)

The values of  $\gamma$  calculated for  $0^\circ$  and  $25^\circ$  from freezing-point measurements (Hartmann and Rosenfeld, Z. physikal. Chem. 1933, 164, 377) are:

$m$	0.001	0.01	0.05	0.1	0.5
$\theta/m$	3.67	3.60	3.519	3.492	3.496
$\gamma_0$	0.966	0.905	0.828	0.791	0.715
$\gamma_{25}$	0.966	0.905	0.828	0.791	0.720

$m$	1.0	2.0	3.0	4.0	5.0
$\theta/m$	3.640	3.864	4.145	4.430	4.708
$\gamma_0$	0.714	0.780	0.852	0.966*	1.097*
$\gamma_{25}$	0.724	0.793	0.909		

\* At f.p. ( $m=4$ ,  $\theta=-17.718^\circ$ ;  $m=5$ ,  $\theta=-23.535^\circ$ ).

The activity coefficients calculated from the e.m.f. of the quinhydrone electrode in nitric acid, suitably corrected (Stonehill, J.C.S. 1943, 647) are practically the same as those for hydrochloric acid at the same concentrations.

The nitric acid molecule is planar (Maxwell and Mosley, J. Chem. Physics, 1940, 8, 738; Forsythe and Giaugue, J. Amer. Chem. Soc. 1942, 64, 48) and the general shape is a triangular  $\text{NO}_3$  with distances N to O of 1.22 Å. in the unshared oxygens and 1.41 Å. for N to the O of the OH radical. The O to H distance is 0.96 Å. The O-N-O angle is  $130^\circ$  for the unshared oxygens and  $115^\circ$  between the N to shared O bond and the other two. The  $\text{NO}_3^-$  ion in crystals of nitrates is also planar (Elliott, *ibid.* 1937, 59, 1380) with the N-O distance 1.21 Å. The  $\text{HNO}_3$  molecule is best interpreted as a resonance hybrid between the two forms (L. Pauling, "The Nature of the Chemical Bond," Ithaca, N.Y., 1940, p. 209):

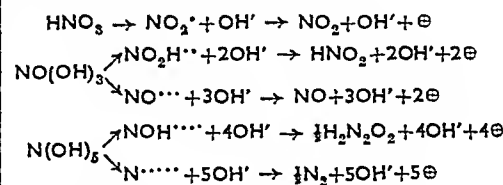


The chemical properties of nitric acid may be summarised by the statement that it is at the same time a strong acid and, at least when concentrated, a strong oxidising agent. The usual methods (rates of hydrolysis of methyl acetate and inversion of cane sugar, freezing-point lowering and conductivity) show that it is a very strong acid. For this reason it has a high heat of neutralisation, 13,680 g.-cal. with sodium hydroxide and 13,770 g.-cal. with potassium hydroxide (J. Thomsen, "Thermochemistry," Longmans, 1908, p. 115), or at infinite dilution 13,705 g.-cal. for sodium hydroxide and 13,700 g.-cal. for potassium hydroxide (Richards and Rowe, J. Amer. Chem. Soc. 1922, 44, 684). The heat of ionisation for  $v$  (kg. containing 1 g.-mol. of  $\text{HNO}_3$ ) = 1.5-6 is 2,800 g.-cal. (Petersen, Z. physikal. Chem. 1893, 11, 174) and for  $v=10$  it is 1,362

g.-cal. (Arrhenius, *ibid.* 1888, 4, 96; 1892, 9, 339).

Nitric acid is readily soluble in ether, in which it has a normal molecular weight, and the distribution coefficient between ether and water has been determined (Bogdan, Z. Elektrochem. 1905, 11, 824; 1906, 12, 489; Hantzsch and Sebaldt, Z. physikal. Chem. 1899, 30, 285). All normal metallic nitrates are soluble in water and there is practically no tendency to complex formation. Some basic salts are sparingly soluble. Some acid salts, e.g.,  $\text{NH}_4\text{NO}_3$ ,  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$ , and the corresponding potassium salts, are known (Groschuff, Ber. 1904, 37, 1486).

In its oxidising actions, nitric acid is capable of reduction to  $\text{HNO}_2$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{N}_2\text{O}_2$ , hydroxylamine, nitrogen, and ammonia, and the reactions with metals may be systematised by postulating an ionisation of  $\text{HNO}_3$  or hypothetical hydrates to give  $\text{OH}'$  ions and cations which lose positive charges to the metal (W. Ostwald, "Principles of Inorganic Chemistry," Macmillan, 1904, p. 638):



The oxidation potential is lowered by the presence of nitrous acid, which, however, catalytically increases the rate of oxidation (Ihle, Z. physikal. Chem. 1896, 19, 577; Ellingham, J.C.S. 1932, 1565); in the electrolysis of the acid between platinum electrodes there are two alternative reactions, (a) reduction to nitrous acid, and (b) evolution of hydrogen, of which (a) is strongly autocatalytic.

Nitric acid is not affected by hydrogen gas at ordinary temperatures or at  $100^\circ$  (Berthelot, Compt. rend. 1898, 127, 27), but is reduced by it to ammonia in presence of platinum sponge (Wagner, Dinglers Polytech. J. 1867, 183, 76). The concentrated acid on slightly warming oxidises boron to boric acid with evolution of NO and nitrogen, carbon to carbon dioxide, and in the cold if finely divided, phosphorus to phosphorous acid and finally to phosphoric acid (when according to Montemartini, Gazzetta, 1898, 28, i, 397, ammonia is also produced). Sulphur is oxidised to sulphuric acid with great readiness if finely divided, selenium to selenious acid, and iodine to iodic acid. In these reactions NO and  $\text{NO}_2$  are evolved. Hydrides are also oxidised: phosphine readily, hydrogen sulphide only if  $\text{NO}_2$  is present (acid of  $\rho$  1.18 free from  $\text{NO}_2$  has no action: Kemper, Annalen, 1857, 102, 342), hydrogen selenide violently (Hofmann, Ber. 1870, 3, 660). Hydrogen bromide at  $0^\circ$  forms bromine and  $\text{NO}_2$ , hydrogen iodide yields iodine and NO ( $\text{HNO}_2$  in dilute solution, Eckstädt, Z. anorg. Chem. 1901, 29, 51) and fuming nitric acid may inflame gaseous HI (Hofmann). Hydrochloric acid forms NOCl and  $\text{Cl}_2$ .

Sulphur dioxide reduces  $\text{HNO}_3$  readily, some

$\text{N}_2\text{O}$  being formed. In presence of dilute sulphuric acid reduction is still more readily effected, with evolution of  $\text{NO}$ , and in presence of concentrated sulphuric acid nitrosyl hydrogen sulphate,  $\text{NO}\cdot\text{HSO}_4$ , is formed: this is produced if sulphur dioxide is passed slowly into well-cooled concentrated nitric acid (Weber, Ann. Phys. Chem. 1867, 130, 277; see p. 532c). Ferrous salts yield  $\text{NO}$ , stannous salts hydroxylamine and ammonia, arsenic trichloride and trioxide form arsenic acid, and antimony trichloride forms antimony pentoxide.

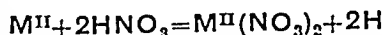
The action of nitric acid on metals is complex. All metals, except pure aluminium, gold, niobium, tantalum, rhodium, iridium, and platinum, are attacked by nitric acid of various concentrations. Some metals commonly dissolved, e.g., iron, may become "passive" in concentrated nitric acid, the rate of solution being then reduced to a small value, and, conversely some metals not alone attacked may dissolve along with another metal in an alloy or amalgam, e.g., an amalgam of 4.64% of platinum and 95.35% of mercury is completely soluble (Tarugi, Gazzetta, 1903, 33, ii, 171).

The action is more rapid when the metal is at rest in the acid than when it is rotated rapidly, which indicates that nitrous acid accumulating around the metal as a result of the attack by the acid exerts an autocatalytic action (Voley, J.C.S. 1889, 55, 361; Hedges, *ibid.* 1930, 561).

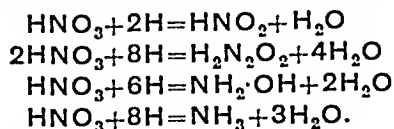
The result of the action is the nitrate of the metal, except in the cases of tin, arsenic, antimony, molybdenum, and tungsten, when an oxide is formed, and the nitric acid is reduced to various products (see above).

With less reactive metals (copper, silver, mercury, bismuth) reduction proceeds only to the stage of nitrous acid or oxides of nitrogen; with more reactive metals (magnesium, zinc, cadmium, tin, manganese, iron, cobalt, and nickel) reduction proceeds to the stages of nitrogen, hydroxylamine, and ammonia, perhaps as a result of reduction by hydrogen as a primary product. Magnesium and manganese with cold, very dilute, nitric acid evolve hydrogen. Zinc and very dilute acid give ammonia; with tin, hydroxylamine is one of the products (Divers, *ibid.* 1883, 43, 443, 455). The products with a given metal may depend on the concentration of the acid (which changes during reaction), the temperature, and the accumulation in solution of the products of reaction; with zinc in intermediate concentrations nitrous oxide and nitrogen may be formed in considerable amounts, and although the chief product of the action of dilute nitric acid on copper is nitric oxide, nitrogen peroxide ( $\text{NO}_2$ ) is formed with concentrated acid, and with acid of moderate concentrations the later portions of gas evolved with copper may contain nitrous oxide and nitrogen (Montemartini, Gazzetta, 1892, 22, i, 250, 277, 384, 397, 426; Atti R. Accad. Lincei, 1892, [v], 1, i, 63; Walker, J.C.S. 1893, 63, 845; Stillmann, J. Amer. Chem. Soc. 1897, 19, 711; Freer and Higley, Amer. Chem. J. 1899, 21, 377; Bijlert, Z. physikal. Chem. 1899, 31, 103; Gladstone, Phil. Mag. 1900, [v], 50, 231; Stansbie, J.S.C.I. 1908, 27, 365; 1909, 28, 268; Rennie, Higgin, and Cooke, J.C.S. 1908, 93,

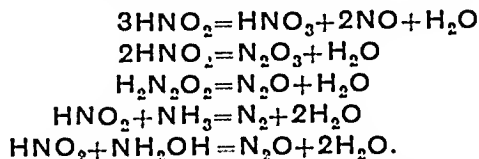
1162; Dunstan and Hill, *ibid.* 1911, 99, 1853) Armstrong and Acworth (*ibid.* 1877, 32, 54; Ellingham, *ibid.* 1932, 1565; cf. Evans, Trans. Faraday Soc. 1944, 40, 120) supposed that in all cases nascent hydrogen is the first product of the action:



and then reduces the excess of nitric acid:



The reduction products may then undergo reactions to form other products:

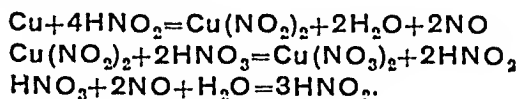


(The objection sometimes raised, e.g., by Hedges, *l.c.*, against the nascent hydrogen theory, that copper does not dissolve in other acids with evolution of hydrogen, is invalid, since this metal dissolves in hot concentrated hydrochloric, hydrobromic, and hydriodic acids with evolution of hydrogen.)

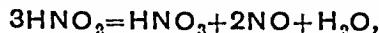
The action of nitric acid on the metals copper, silver, mercury, and bismuth is greatly accelerated by the presence of nitrous acid, a fact noticed by Millon (J. Pharm. Chim. 1842, [iii], 2, 179; Ann. Chim. Phys. 1842, [iii], 6, 73, 95; 1843, [iii], 7, 320) and explained by him as follows:

"The nitrous acid forms nitrites . . . which are destroyed by the nitric acid as fast as they are formed; this destruction gives rise to nitric oxide which in presence of nitric acid reforms nitrous acid whence a new attack and a new destruction result."

Thus:



The nitrous acid so continuously produced will decompose when it reaches a certain concentration:

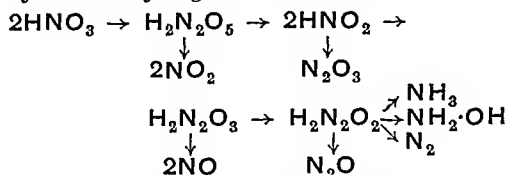


nitric oxide being evolved. With concentrated nitric acid, the product is  $\text{NO}_2$ , formed by the reaction:  $2\text{HNO}_3 + \text{NO} = 3\text{NO}_2 + \text{H}_2\text{O}$ . Millon's theory was confirmed and extended by Voley (Proc. Roy. Soc. 1890, 46, 216; 1890, 48, 458; 1893, 52, 27; Phil. Trans. 1891, 182, 279, 319; J.S.C.I. 1891, 10, 204).

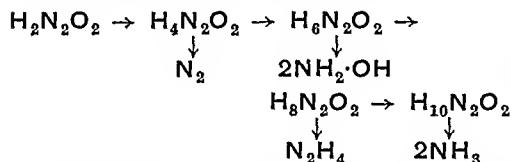
Voley showed that if nitrous acid is removed by adding urea or hydrogen peroxide, the diluted nitric acid does not act upon copper; the action of these substances is evanescent, but if hydrazine hydrate is added, the metal and 50% nitric acid can remain in contact for one or two days without action. The copper dissolves in ordinary nitric acid to form first of all a green solution of copper nitrite; when all the metal is dissolved this becomes blue from conversion into

nitrate. Fuming concentrated nitric acid containing dissolved  $\text{NO}_2$  is without appreciable action on copper (the yellow acid turns green), but if a little water is added nitrous acid is formed and the copper dissolves in a violent reaction, abundant red fumes being evolved.

Bancroft (J. Physical Chem. 1924, 28, 475, 973, with bibliography) postulated a dynamic equilibrium  $\text{HNO}_3 + \text{HNO}_2 \rightleftharpoons \text{N}_2\text{O}_4 + \text{H}_2\text{O}$ , and supposed that in the moments of change the  $\text{HNO}_3$  is in some peculiar state which makes it more reactive, e.g., towards hydrogen. Milligan (*ibid.* 1924, 28, 544, 794) postulated the following series of reduction products formed by nascent hydrogen:



$\text{H}_2\text{N}_2\text{O}_2$ , however, is *not* reduced as postulated in the final stages, although Joss (*ibid.* 1926, 30, 60) elaborated this part of the scheme:



He considered the hypothetical *nitrosic acid*,  $\text{H}_2\text{N}_2\text{O}_5$ , as the intermediate product in a state of dynamic equilibrium:

$\text{HNO}_3 + \text{HNO}_2 \rightleftharpoons \text{H}_2\text{N}_2\text{O}_5 \rightleftharpoons 2\text{NO}_2 + \text{H}_2\text{O}$ , and as being the real depolariser, nitrous acid playing the part of a catalyst in activating the nitric acid.

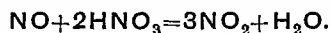
Alloys of copper and zinc containing more than 48% of copper dissolve as a whole in nitric acid. With less copper, the zinc either dissolves faster than the copper or precipitates this metal from the solution, and more copper dissolves when the solutions are shaken than when at rest (Stansbie, J.S.C.I. 1913, 32, 1135).

Electrolytic reduction of nitric acid yields first nitrous acid and finally ammonia (Schönbein, Ann. Phys. Chem. 1839, 47, 563; Brester, Chem. News, 1868, 18, 144; Bloxam, *ibid.* 1869, 19, 289). The nature of the product depends on the temperature, current strength, material of the cathode, cathodic potential, and acidity or alkalinity of the solution, and two different reactions may occur, evolution of hydrogen or reduction to nitrous acid (Ellingham, J.C.S. 1932, 1565). With a mercury cathode only hyponitrite is formed (Zorn, Ber. 1879, 12, 1509) and with a copper cathode ammonia (Ulsch, Z. Elektrochem. 1897, 3, 546). On electrolysis of 40%  $\text{HNO}_3$  containing 1% of dissolved nitrous gases almost pure  $\text{NO}$  is evolved at the cathode (Meister, Lucius, and Brüning, B.P. 10522, 1911; Müller *et al.*, Z. Elektrochem. 1903, 9, 955, 978; 1905, 11, 509; Ber. 1905, 38, 778, 1190; Tafel, Z. anorg. Chem. 1902, 31, 289). Tafel found that although nitric acid is reduced only to hydroxylamine by mercury or well-

amalgamated electrodes, copper electrodes reduce it only to ammonia.

For the detection and estimation of nitric acid and nitrates, see Vol. II, 598c, 664a, 673c, 687d, 688d V, 327d; this Vol. p. 588b (also Reichard, Chem.-Ztg. 1906, 30, 790; Howard and Chick, J.S.C.I. 1909, 28, 53; Schmidt and Lump, Ber. 1901, 43, 787, 794).

Fuming Nitric Acid is a yellow or orange-red fuming liquid with powerful oxidising properties, prepared by dissolving  $\text{N}_2\text{O}_3$  or  $\text{N}_2\text{O}_4$  in concentrated nitric acid, distilling potassium nitrate with potassium bisulphate, or potassium nitrate and some starch with concentrated sulphuric acid, or adding paraformaldehyde or kieselguhr soaked in formaldehyde to concentrated nitric acid (Vanino, Ber. 1899, 32, 1392). It contains free  $\text{NO}_2$  (Marchlewski, Z. anorg. Chem. 1892, 1, 368). Nitric oxide reacts with concentrated nitric acid as follows:



The yellow acid on addition of water becomes green, blue (from formation of  $\text{N}_2\text{O}_3$ : see p. 522c) and finally colourless (Marchlewski and Liljensztern, *ibid.* 1892, 2, 18; 1894, 5, 288). For densities of fuming nitric acid, see Lunge and Marchlewski, Z. angew. Chem. 1892, 5, 10. Fuming nitric acid has been used in quantitative organic analysis (Carius, Ber. 1870, 3, 697).

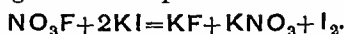
#### HALIDES OF NITRIC ACID.

Nitryl Fluoride,  $\text{NO}_2\text{F}$ , formed by the action of excess of fluorine on nitric acid at the temperature of liquid air, is a gas, b.p.  $-72.4^\circ$ , m.p.  $-166^\circ$ , with a density 2.17–2.31 (air=1) agreeing with that (2.26) calculated for  $\text{NO}_2\text{F}$ . It does not combine with hydrogen, sulphur, or carbon, but attacks boron, silicon, phosphorus, arsenic, antimony, iodine, alkali and alkaline earth metals, aluminium, iron, and mercury. It reacts with water:

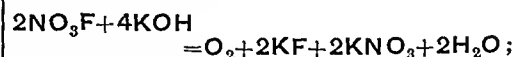


and with many organic compounds (Moissan and Lebeau, Compt. rend. 1905, 140, 1573; Ruff *et al.*, Z. anorg. Chem. 1932, 208, 293).

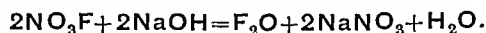
Pernitryl Fluoride or Fluorine Nitrate,  $\text{NO}_3\text{F}$ , is formed as a colourless explosive gas, b.p.  $-42^\circ$ , by the action of fluorine on concentrated nitric acid (Cady, J. Amer. Chem. Soc. 1934, 56, 2635; Yost and Beerbower, *ibid.* 1935, 57, 782; Ruff and Kwasnik, Angew. Chem. 1935, 48, 238). It is a strong oxidising agent, liberating iodine from potassium iodide:



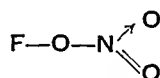
It is hydrolysed by 20% potassium hydroxide solution as follows:



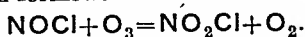
with 2% sodium hydroxide solution fluorine monoxide is formed:



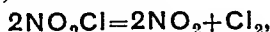
The structure may be



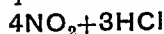
Nitryl Chloride,  $\text{NO}_2\text{Cl}$ , is formed by the reaction between nitrosyl chloride and ozone, cooling the product in liquid air, and removing the oxygen formed:



It is a colourless gas, condensing at  $-15^\circ$  to a colourless liquid,  $\rho$  1.37, f.p.  $-145^\circ$ . Its thermal decomposition,



appears to be a reaction of the first order (Schumacher and Spronger, Z. anorg. Chem. 1929, 182, 139; Z. Elektrochem. 1929, 35, 653; Z. physikal. Chem. 1931, B, 12, 115). Small quantities of  $\text{NO}_2\text{Cl}$  are formed by the reaction:

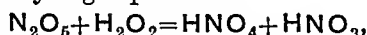


(Müller, Annalen, 1862, 122, 1; Odet and Vignon, Compt. rend. 1870, 70, 96) and by other reactions (Noyes, J. Amer. Chem. Soc. 1932, 54, 3615), although its existence was denied by Gutbier and Lohmann (J. pr. Chem. 1905, [ii], 71, 182). The existence of nitryl bromide (Hasenbach, *ibid.* 1871, [ii], 4, 1) has not been confirmed.

**Pernitrous Acid.**—Raschig (Z. anorg. Chem. 1904, 17, 1417; Ber. 1907, 40, 4585) found that a mixture of hydrogen peroxide and acidified sodium nitrite solution liberates bromine from potassium bromide solution, whereas neither solution separately liberates bromine. He supposed that *pernitric acid*,  $\text{HNO}_4$ , was formed, a view also adopted by Pollak (Z. anorg. Chem. 1925, 143, 143), whilst Trifenev (*ibid.* 1922, 124, 123, 136) thought the product was  $\text{N}_2\text{O}_6$ ,  $n\text{H}_2\text{O}$  or

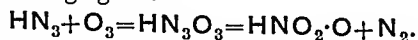


D'Ans and Friederich (Z. Elektrochem. 1911, 17, 849; Z. anorg. Chem. 1912, 73, 325) reported that explosive  $\text{HNO}_4$ , smolling of hypochlorous acid, is formed by dissolving  $\text{N}_2\text{O}_5$  in anhydrous hydrogen peroxide:



but Schmidlin and Massini (Ber. 1910, 43, 1162) found that ozone is evolved, even with strong cooling, and on dilution only unchanged hydrogen peroxide was detected. The supposed formation of  $\text{N}_2\text{O}_6$  by the action of fluorine on dilute nitric acid, and of  $\text{HNO}_4$  by the action of fluorine on dilute sodium nitrite solution (Fichter and Brunner, Helv. Chim. Acta, 1929, 12, 305) must be regarded as requiring confirmation.

Schmidlin and Massini (*l.c.*) regarded the supposed pernitric acid as really pernitrous acid,  $\text{HNO}_2 \cdot \text{O}$  or  $\text{O}=\text{N}-\text{O}-\text{OH}$ , isomeric with nitric acid  $\text{O}_2\text{N}-\text{OH}$  but possessing a peroxido group  $-\text{O}-\text{O}-$ , and this view is supported by the experiments of Gleu and co-workers (Z. anorg. Chem. 1929, 179, 233; 1935, 223, 305). It was found that when oxygen containing 10% of ozone is passed into N. sodium azido solution an unstable orange solution is formed which is an oxidising agent:



Pernitrous acid is also the product of the oxidation of nitrous acid by hydrogen peroxide.

To a mixture of 2 mol. of sodium nitrite and more than 2 mol. of hydrogen peroxide, with a

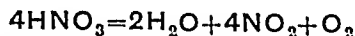
large amount of ice, 1 mol. of 2N. sulphuric acid was added, and after two seconds a large excess of sodium hydroxide solution. An intensely yellow solution was formed. In this, the excess of hydrogen peroxide was determined by titrating a portion of the alkaline solution with 0.1N. sodium hypochlorite solution with ten drops of 0.1N. potassium iodide until the colour of Ruthenium Red indicator was discharged. The active oxygen was then determined by immediately adding excess of 0.1N. sodium arsenite and back-titrating with hypochlorite, with Ruthenium Red indicator. The nitrite was determined by reduction to ammonia with vanadyl sulphate, which does not reduce nitrate, and distilling into standard acid. The ratio of nitrite radical to active oxygen was found to be 1:1, hence the substance was supposed to be pernitrous acid,  $\text{HNO}_2 \cdot \text{O}$ .

#### THE MANUFACTURE OF NITRIC ACID.

Until the widespread adoption of synthetic processes in recent times, the industrial methods for the preparation of nitric acid followed fairly closely those used in the sixteenth and seventeenth centuries for the production of *aqua fortis* for parting gold and silver, and some still older processes used by the alchemists were regularly patented. In the last edition of this Dictionary the article on nitric acid could say that the retort process was "still the most important," and could point out, rather naïvely, that "for most uses the nitric acid yielded by [ammonia oxidation] is too weak and must be concentrated, an expensive process at best." There were, in fact, large installations then producing synthetic concentrated acid at a much lower cost than by the retort process, and as the latter is now abandoned except in rather primitive conditions, a brief account of it will suffice.

In this process, approximately equal weights of sodium nitrate and 66°Bé. sulphuric acid are heated in cast-iron retorts. The fused residue consists of a mixture of sodium sulphate and sodium hydrogen sulphate, and if over-heated may also contain sodium disulphate ( $\text{Na}_2\text{S}_2\text{O}_7$ ). This residue is discharged into iron pans, where it solidifies to a compound (Faust and Esselmann, Z. anorg. Chem. 1926, 157, 290)  $\text{Na}_3\text{H}(\text{SO}_4)_2$  or  $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$  known as *nitre-cake*; or it may be run into the pan of a hydrochloric acid furnace, where it is converted into salt-cake by reacting with salt.

The vapour from the retort, especially at the beginning and end of the process, contains nitrogen peroxide from the decomposition of nitric acid by heat (Carius, Annalen, 1873, 169, 273):



which partly dissolves in the acid. The lowering of the partial pressure by dilution with air facilitates this reaction. The water formed in this reaction and that originally in the raw materials, condenses with the nitric acid. The remaining gas passes from the condenser to the absorption towers along with some uncondensed nitric acid vapour.

The first portions of distillate are the most con-

centrated, the acid becoming weaker as the distillation proceeds, until at the end it is almost pure water. The greatest evolution of nitrogen peroxide also occurs in the beginning, and it is usually prevented from dissolving in the acid by so condensing that the acid is removed hot from the system.

The retorts are vertical cast-iron pots in a brick setting. The cast iron is not attacked by nitric acid vapour, or appreciably corroded by the sulphuric acid in the charge. Fig. 8 shows one type of retort and setting, arranged for coal firing. Gas firing is also used.

Sodium nitrate and sulphuric acid are introduced at A, and the nitric acid distills off at B. At the end of the distillation the fused nitre-cake is run off through C.

Many forms of water-cooled condensers have

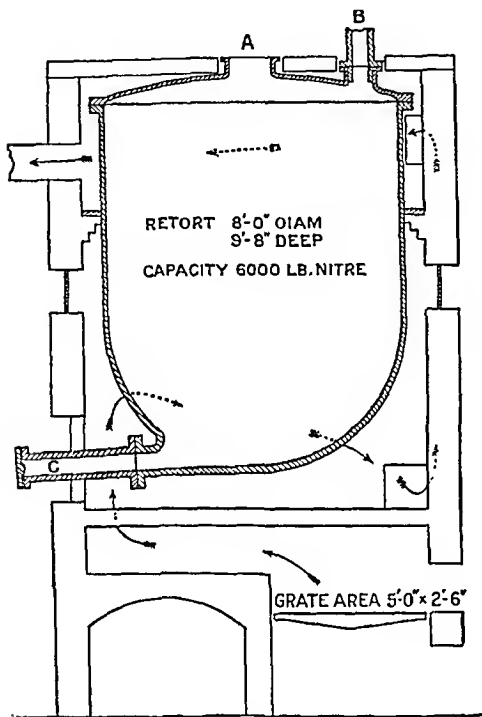


Fig. 8.

been used, including the glass condenser of Hart (U.S.P. 525761, 1894; B.P. 17289, 1894) and S-bend condensers made of silica or of silicon-iron alloys.

A Hart condenser (Fig. 9) consists of two upright manifolds of chemical-ware or silicon-iron, connected by parallel glass tubes 3 in. in diameter and 6 ft. long, packed into the manifolds with putty of oil-ground white-lead, 10 lb., red-lead, 1 lb., linseed oil, 3 gal., and asbestos fibre to give proper consistency. Water trickles over the outside of the tubes from the pipe A, and is kept from splashing by wooden guides hung between the tubes and shown in detail at B and in cross section at C. The hot water passes through the trough D to the drain E.

The tube breakage may amount to about 100 per retort per year. It is heaviest with weak charging sulphuric acid. Broken tubes may be replaced while running.

The S-bend condenser (Fig. 10) is a Y-tube branching from the top of the bleacher (shown on the lower left-hand side of Figs. 9 and 10) to two parallel series of S-bends, 6 in. in diameter and 6 ft. long.

To remove oxides of nitrogen it was formerly

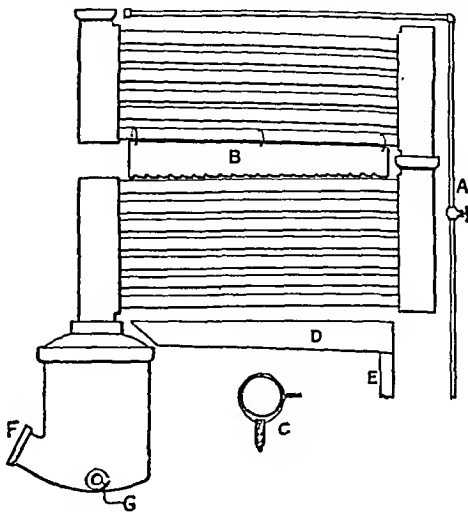


Fig. 9.

the practice to warm the acid and blow a current of air through it. This separate operation is avoided (Skoglund, U.S.P. 591087, 1897; B.P. 22816, 1897) by allowing the hot condensed acid to reflux through a bleacher. It encounters hot gas from the retort, which further heats it, driving out the dissolved nitrogen peroxide.

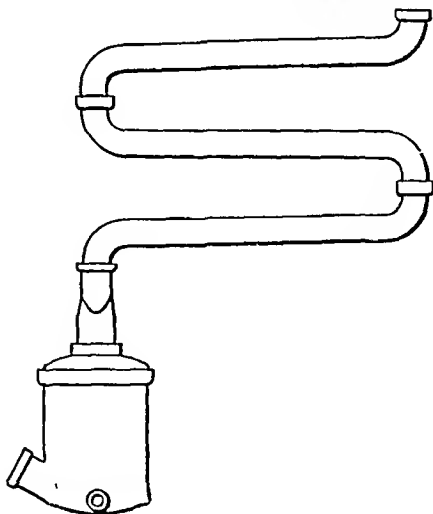


Fig. 10.

The acid running from the bleacher contains, on an average, about 1% of  $\text{NO}_2$ .

The gas from the retort enters at F (Fig. 9) rises through the packing in the bleacher, and condenses in the condenser. The condensate drains back through the bleacher in counter-current to the gases and emerges at G.

From 6-10% of the nitrogen content of the nitrate passes the condenser in the form of

nitrogen peroxide, and in the absorption system this is converted into nitric acid.

The absorption system consists of a series of chemical stone-ware towers with acid-proof packing, in which the gas is scrubbed with dilute nitric acid. The strongest gas comes in contact with the strongest acid, and the weakest gas with almost pure water. In these towers the following reactions occur :

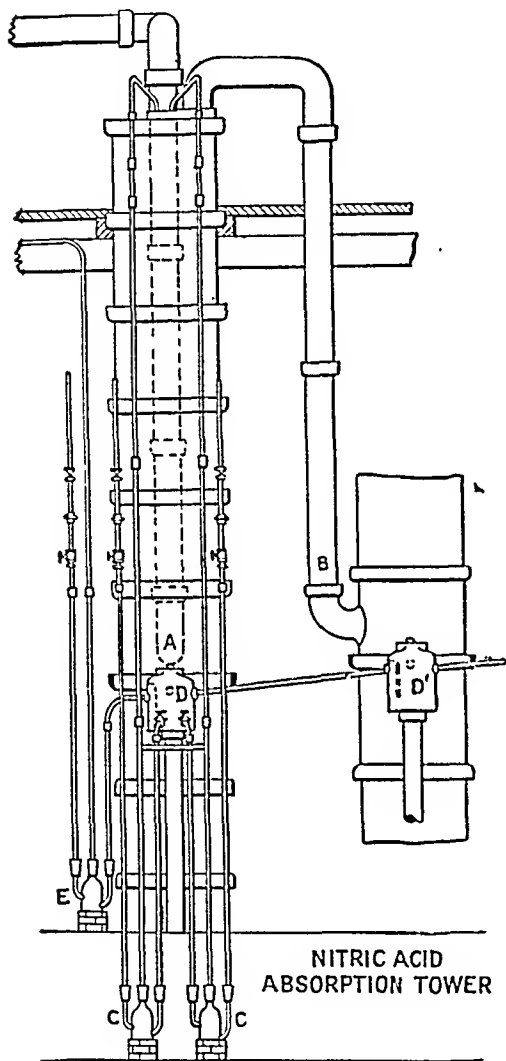
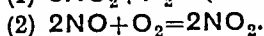
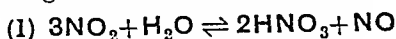


FIG. 11.

The first is established practically instantly (Burdick and Freed, *J. Amer. Chem. Soc.* 1921, 43, 518), while the second is a slow reaction in its later stages (Burdick, *ibid.* 1922, 44, 244). Owing to the limited reaction space in the towers, this reaction is never completed, and 95% conversion of the  $\text{NO}_2$  to dilute nitric acid has been considered good practice.

The absorption tower (Fig. 11) consists of 6 sections of chemical-ware about 30 in. in diameter and 30 in. high. The bottom section rests in a saucer mounted on a pedestal. The gas enters the tower at A, rises through the packing (usually pottery rings), and leaves

through B. Acid is continually circulated over the tower by Pohle air-lifts C, supplied with acid from the equaliser pot D. The acid draining from the towers enters this pot from behind; any excess above that in circulation, which may enter from the next equaliser pot D', or be formed in the tower, is removed continually by the air-lift E.

In a series of such towers, each is set higher than its predecessor, so that weak acid may drain towards the acid exit. Draught is maintained in the exit from the last tower.

The best charging sulphuric acid to use with dry nitre is 92.5% (Winteler, *Chem.-Ztg.* 1905, 29, 820). With wet nitre the strength of the acid is increased proportionally to the water content. Either stronger or weaker acid results in a less concentrated distillate.

With a ratio of  $\text{H}_2\text{SO}_4:\text{NaNO}_3=1:1$  and acid of the above strength the plant produces a distillate of 90-92%  $\text{HNO}_3$ , constituting about 90% of the acid made. The remaining 10% is weaker, containing 60-80% of  $\text{HNO}_3$ . The overall yield is 94-96%, the nitre-charge acidity varying from 27-31%  $\text{H}_2\text{SO}_4$ , and the coal consumption about 0.185 lb. per lb. 100%  $\text{HNO}_3$  with gas firing and about 0.325 with direct firing. Using a nitre charge of 5,000-5,300 lb. the time of a complete cycle is 18-24 hours (Ministry of Munitions, Department of Explosives Supply, "Report on the Statistical Work of the Factories Branch," H.M. Stationery Office, London, 1919; "Preliminary Studies for H.M. Factory, Gretna," H.M. Stationery Office, London, [1919]).

In the U.S.A. (Zeisberg, *Chem. Met. Eng.* 1921, 24, 443) the cycle of operations with a 7,000 lb. nitre charge required only 12 hours and the yield was better, approximately 99%. The coal consumption with direct firing was 0.222 lb. per lb. of 100%  $\text{HNO}_3$  with continuous operation, and 0.265 lb. with one-shift operation. The labour was 1.9 man-hours per 1,000 lb. of  $\text{HNO}_3$  with single-shift, and 1.4 man-hours with continuous operation. The average strength of the whole output was 88-90%  $\text{HNO}_3$  (including tower acid) with about 1% of  $\text{NO}_2$ .

*Vacuum Processes.*—In order to avoid thermal decomposition of the nitric acid, Valentiner (G.P. 63207, 1891; B.P. 610, 1892; 19192, 1895; 4254, 1907; G. Lunge, "Sulphuric Acid and Alkali," Gurney and Jackson, 1913, Vol. I, p. 173; J. R. Partington, "The Alkali Industry," Baillière, 1925, pp. 195-216, 229 (bibl.) including other processes) carried out the distillation in vacuum. The process was developed in Germany by Frischer, who increased the size of the apparatus and used a rotary liquid-seal pump instead of the older reciprocating pump, and in the U.S.A. by Hough (E. C. Wordon, "Technology of Cellulose Esters," Spon, 1921, Vol. I, ii, p. 34), who introduced a stirring device in the retort.

Commercial nitric acid made from Chile nitre contains various impurities, particularly chlorine and sometimes traces of organic compounds, such as tetranitromethane, monochlorotrinitromethane, and dichlorodinitromethane (Crawford, *J.S.C.I.* 1922, 41, 321r).



### NITROGEN, ATMOSPHERIC, UTILISATION OF.

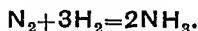
Nitrogenous substances, particularly nitrates and ammonium salts, are used as plant manures. The natural formation of combined nitrogen is insufficient to keep pace with an increasing population's food requirements (Sir W. Crookes, "The Wheat Problem," 3rd ed., Longmans, 1917). According to Russell (J.S.C.I. 1918, 37, 45a) 1 lb. of combined nitrogen properly used in the soil will yield enough food to supply a man for about five days. Normally, a plant takes up nitrogen in the form of nitrates, and the most efficient nitrogenous fertilisers are the nitrates of potassium, calcium, and sodium, probably in the order given. Other nitrogen compounds are first oxidised to nitrates in the soil. Ammonia is rapidly oxidised to nitrates by soil bacteria, and ammonium salts are converted into nitrates before the plant is ready for all the nitrogen supplied. Protein nitrogen, amino-acid nitrogen, and amide-nitrogen, present in farmyard manure, are also rapidly so oxidised. Calcium cyanamide is first converted into ammonia and then nitrate. Other nitrogen compounds, such as diazo-compounds, nitro-compounds, and ring-compounds, are (as far as is known) useless as fertilisers. The relative values of combined nitrogen in various forms are: nitrate 100; ammonia, 95; cyanamide, 85-90 or more; protein, 70-80.

The natural sources of combined nitrogen are two. First, electrical discharges in the atmosphere cause the union of oxygen and nitrogen, with the ultimate production of nitrates and nitrites. (See, however, Moore, J.C.S. 1921, 119, 1555; Reynolds, Nature, 1923, 112, 396.) By this means, it is estimated, every acre of ground in Great Britain is enriched annually to the extent of 11 lb. of combined nitrogen. In the tropics, where thunderstorms are more frequent, the amount is larger.

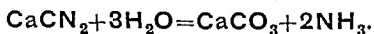
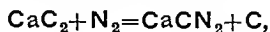
The second natural source of combined nitrogen is the fixation of nitrogen by organisms in the soil (see NITROGEN FIXATION, BIOLOGICAL, this Vol., p. 583a).

The nitrogen of the atmosphere over every square mile of the earth amounts to about 20 million tons. The methods which are, or have been, in use, or proposed for use, in "fixing" or utilising atmospheric nitrogen, by converting it into compounds, include the following:

1. The *direct synthesis of ammonia* from nitrogen and hydrogen gases:



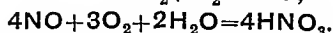
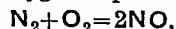
2. The reaction between nitrogen and calcium carbide, leading to the formation of calcium cyanamide,  $\text{CaCN}_2$ , which may be used directly as a fertiliser or hydrolysed with the formation of ammonia:



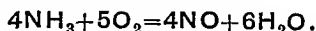
3. The *formation of metallic nitrides or cyanides* by various processes.

4. The *direct synthesis of nitric oxide* in the electric arc, followed by the oxidation of this to

nitric acid by free oxygen in presence of water:



5. The *conversion of ammonia to nitric oxide by catalytic oxidation* and subsequent treatment of the nitric oxide as in (4):



The most important processes are (1) and (5), which provide the basis of the modern nitrogen industry.

### SYNTHETIC AMMONIA.

Experiments on the union of nitrogen and hydrogen, with formation of ammonia, on passing *electric sparks* through a mixture of the two gases, were made by Regnault in 1845, by Deville in 1865, and by H. B. Dixon in 1888 (cf. Briner and Mettler, J. Chim. phys. 1908, 6, 137; Briner and Kahn, *ibid.* 1914, 12, 534; Briner and Baerfuss, Helv. Chim. Acta, 1919, 2, 95, 162). An equilibrium yield of ammonia at ordinary temperature is attained by circulating a nitrogen-hydrogen mixture round a lead cathode in a low pressure discharge tube (Jolibois and Olmer, Compt. rend. 1936, 202, 1268). The synthesis of ammonia by the *silent electric discharge*, discovered by Donkin in 1873, was confirmed by Le Blanc and Davies (Z. physikal. Chem. 1908, 64, 657). The supposed production of ammonia by passing a mixture of nitrogen and hydrogen over a catalyst (Swindells and Lancaster, B.P. 2563 and 3148, 1876; Johnson, J.C.S. 1881, 39, 128, 130) was due to the reduction of nitrogen oxides, not removed by ferrous sulphate solution, in the nitrogen prepared from ammonium nitrite (Wright, *ibid.* 1881, 39, 357; Mond, J.S.C.I. 1889, 8, 505), these oxides, as Dulong and Thenard (Ann. Chim. Phys. 1923, [ii], 23, 440) found, being readily reduced to ammonia in presence of platinum. Processes in which ammonia was synthesised by passing nitrogen and hydrogen over heated iron were also shown to depend on the presence of iron nitride in the iron, and the first genuine formation of traces of ammonia at atmospheric pressure with a pure iron catalyst was probably achieved by Perman and Atkinson (Proc. Roy. Soc. 1904, 74, 110; 1905, 76, 167) and almost simultaneously by Haber and Van Oordt (Z. anorg. Chem. 1905, 44, 341), and White and Melville (J. Amer. Chem. Soc. 1905, 27, 373).

Nernst (Z. Elektrochem. 1907, 13, 521; 1910, 16, 96) and his assistant Jost (Z. anorg. Chem. 1908, 57, 414; Z. Elektrochem. 1908, 14, 373), were the first to work under pressure (up to 30 atm.), and thus corrected Haber's figures for the equilibrium (Rossignol, Ber. 1907, 40, 2144). This development was carried further by Haber and his pupils (Haber and Le Rossignol, Z. Elektrochem. 1913, 19, 53; Haber, Ponnaz, and Tamaru, *ibid.* 1915, 21, 89; Haber and Maschke, *ibid.* 128; Haber and Greenwood, *ibid.*, p. 241). In 1910 the technical development was taken over by the Badische company, and in the perfecting of the technical details a leading part was taken by C. Bosch, a relative of Haber.

As a catalyst, Haber first used metallic osmium, but this is too expensive; he then used uranium or crude uranium carbide. Nernst then found that, although pure iron is relatively inactive as a catalyst, its activity is greatly enhanced by the addition of other substances, first called in the Badische patents by the name *promoters* or *activators*; in this field valuable researches were carried out by Alwin Mittasch (Ber. 1929, 59, 13; A. Mittasch and E. Theis, "Grenzflächenkatalyse," Berlin, 1932; A. Mittasch, "Kurze Geschichte der Katalyse in Praxis und Theorie," Berlin, 1939) for the Badische company, and by American workers in the U.S. Government Fixed Nitrogen Research Laboratory (Larson and Brooks, Ind. Eng. Chem. 1926, 18, 1305; Almquist and Crittenden, *ibid.*, p. 1307; Almquist, J. Amer. Chem. Soc. 1926, 48, 2820). As a result of X-ray examination of iron catalysts promoted by alumina, it appears that the active material is  $\alpha$ -iron in a spinel-like combination  $\text{Al}_2\text{FeO}_4$  (Wyckoff and Crittenden, *ibid.* 1925, 47, 2866), and similar results were found for other iron catalysts (*see below*).

Synthetic ammonia was first made on the industrial scale in Germany. The Badische Co. (later the I.G. Farbenindustrie) erected large plants at Oppau and Merseburg. The Oppau works, forming practically a continuation of the Badische factory at Ludwigshafen, commenced in 1913 with a capacity of 20 tons of ammonia per day, increased to 200 tons in 1914-18. It is said to have cost £15,000,000. A part of the works was destroyed by an explosion in 1921 (J.S.C.I. 1921, 40, 381x). The Leuna works at Merseburg (Halle) was erected since 1916 with a capacity of 800 tons of ammonia per day. The combined output of Oppau and Leuna in 1932 was one million metric tons of combined nitrogen per annum (Ullmann, "Enzyklopädie der technischen Chemie," 2nd ed., Vol. IX, p. 720).

The number of catalyst materials specified in the Badische and other later patents (*e.g.*, G.P. 265295, 1912) is very large, but as far as is known all the catalysts now in use consist of some form of activated iron (on catalysts, *see, e.g.*, J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, London, 1928, pp. 148 *et seq.*; S. J. Green, "Industrial Catalysis," Benn, 1928, pp. 318 *et seq.*, 334 *et seq.*; Frankenburg and Dürr, in Ullmann, "Enzyklopädie der technischen Chemie," 2nd ed., Vol. VI, pp. 436 *et seq.*; O. Kausch, "Die Kontaktstoffe der katalytischen Herstellung von Schwefelsäure, Ammoniak und Salpetersäure," Halle, 1931, pp. 85 *et seq.*, 172 *et seq.*; E. Sauter, "Heterogene Katalyse," Leipzig, 1930; Larson *et al.*, Chem. Met. Eng. 1922, 26, 493, 555, 558, 647, 683; Larson and Richardson, Ind. Eng. Chem. 1925, 17, 971; Almquist and Black, J. Amer. Chem. Soc. 1926, 48, 2814, 2820 (poisoning by oxygen); Almquist and Dodge, Chem. Met. Eng. 1926, 33, 89; Mittasch *et al.*, Z. Elektrochem. 1928, 34, 159, 829; Z. anorg. Chem. 1928, 170, 193; Eisenhut and Kaupp, Z. physikal. Chem. 1928, 133, 456; Kunsman, J. Amer. Chem. Soc. 1929, 51, 688; Finzel, *ibid.* 1930, 52, 150; Emmett and Brunauer, *ibid.* 1930, 52,

2682 (poisoning by water); Emmett, Hendricks, and Brunauer, *ibid.* 1930, 52, 1456; Mittasch, Z. Elektrochem. 1930, 36, 569; Keuncke, *ibid.* 1930, 36, 690 (Ni-Mo); Gluud, Klempt, Schonfelder, and Riese, Ber. Ges. Kohlentechn. 1930, 3, 52, 96, 170; Mittasch and Keuncke, Z. physikal. Chem. Bodenstein Festb. 1931, 574; Brunauer, Jofferson, Emmett, and Hendricks, J. Amer. Chem. Soc. 1931, 53, 1778; Winter, Z. physikal. Chem. 1931, B, 13, 401; Frankenburg, Z. Elektrochem. 1933, 39, 45, 97, 269; Kröger, *ibid.* 1933, 39, 670; Epshtein and Upolovnikov, J. Chem. Ind. Moscow, 1933, 10, No. 2, 41; Emmett and Brunauer, J. Amer. Chem. Soc. 1934, 56, 35; Lachinov and Telegin, J. Chem. Ind. Moscow, 1934, 12, 31; Emmett and Brunauer, J. Amer. Chem. Soc. 1937, 59, 1553; Brunauer and Emmett, *ibid.* 1940, 62, 1732; Temkin and Pyzhev, Acta Physicochim, U.R.S.S. 1940, 12, 327; Lovo and Emmett, J. Amer. Chem. Soc. 1941, 63, 3297; Emmett and Kummer, Ind. Eng. Chem. 1943, 38, 677).

Pure iron does not form a nitride directly with nitrogen (Mittasch and Frankenburg, Z. physikal. Chem. 1928, 139, 386), but nitrides ( $\text{Fe}_3\text{N}$ ,  $\text{Fe}_2\text{N}$ ,  $\text{FeN}$ ) are formed with ammonia, and these react with hydrogen to form ammonia (Emmett and Love, J. Amer. Chem. Soc. 1933, 55, 4043). Intermediate surface nitrides are postulated by Messner and Frankenburg (Z. physikal. Chem. Bodenstein Festb. 1931, 593).

Usatschov (J. Phys. Chem. Russ. 1940, 14, 1246) supposes that adsorption of hydrogen is the primary process: the catalyst surface becomes saturated with ammonia, leaving only the active spots available for acceleration of the synthesis reaction (*cf.* Koshenova and Kagan, *ibid.* 1940, 14, 1250). The adsorption of nitrogen and hydrogen on iron-molybdenum catalysts, with and without alumina, has been studied (Roiter, Acta Physicochim. U.R.S.S. 1936, 4, 145), also the catalytic decomposition of ammonia by metals (Bodenstein and Kranendieck, Nernst Festschrift, 1912, 99; J.C.S. 1912, 102, ii, 1155; Hinshelwood and Burk, *ibid.* 1925, 127, 1105; Schwab, Z. physikal. Chem. 1927, 128, 161; 1928, 131, 446).

Morozov and Kagan (Acta Physicochim. U.R.S.S. 1938, 8, 549) postulate: (i) chemisorption of nitrogen and hydrogen, (ii) hydrogenation of nitrogen, (iii) desorption of ammonia.

Catalysts are formed, *e.g.*, from ferrous-ferric oxide produced by combustion of iron in oxygen (Claudio, B.P. 153254, 1919), sometimes under pressure, preferably without contact with crucibles, or in magnesia crucibles with the addition of 5-10% of limo (a process used for purifying iron by Troost, Bull. Soc. chim. 1868, [ii], 9, 250), the fused mass being afterwards broken up and remolten with oxides of potassium and aluminium as promoters; or by burning molybdenum steel in oxygen (Larson and Brooks, Ind. Eng. Chem. 1926, 18, 1305; Larson and Richardson, *ibid.* 1925, 17, 971; Brahm, *ibid.* 1922, 14, 791). Excess of ferrous oxide in the combustion product over the composition  $\text{Fe}_3\text{O}_4$  of magnetite is injurious. For an iron catalyst, nickel and cobalt are practically without promotive action; at 550° tungsten and molyb-

denum are most effective, whilst at 450° iron alone or iron-molybdenum give the best results, but the activity of iron falls off rapidly, especially at higher temperatures (for molybdenum mixed catalysts, see Mittasch and Keuneecke, Z. physikal. Chem. Bodenstein Festb. 1931, 574). Oxides of aluminium, silicon, zirconium, thorium, and cerium are active, but the promoter action is most pronounced with basic and acidic oxides combined, e.g.,  $K_2O$  with  $SiO_2$ ,  $Al_2O_3$ , or  $ZrO_2$ . A mixture of 1%  $K_2O$  and 3%  $Al_2O_3$  with iron gave 13.6% ammonia at 100 atm., but  $K_2O$  alone depressed the activity of iron (Larson and Lazote Inc., U.S.P. 1667322, 1928; Larson and Lamb, U.S.P. 1489497, 1510598, 1924; Greathouse, U.S.P. 1618004, 1927). Artificial magnetite is superior to natural as a catalyst (Telegin and Sidorov, J. Appl. Chem. Russia, 1938, 11, 1064; cf. Kamzolkin, Livschitz, and Koshenova, J. Chem. Ind. Russ. 1935, 12, 687).

Among a number of catalysts tested, the greatest stability and activity was found with  $Fe_3O_4$  with 1.5% of  $K_2O$  and 3% of  $Al_2O_3$  (Latschinov and Telegin, *ibid.* 1934, 10, No. 12, 31; cf. Gauchman and Reuter, J. Phys. Chem. Russ. 1939, 13, 593). The activity of  $Fe_3O_4$  is greatly increased by  $Al_2O_3$ , which probably enhances the surface activity (Kobozev, Jerofeef, Kaverin, and Bogojavlenskaja, Acta Physicochim. U.R.S.S. 1934, 1, 483; Telegin, Sidorov, and Schupulenko, J. Appl. Chem. U.S.S.R. 1940, 13, 823). Titanomagnetite fused with potassium aluminate gives an active catalyst (Geid, J. Chem. Ind. U.S.S.R. 1934, 10, No. 9, 46; Kamzolkin and Avdeeva, *ibid.* No. 10, 48). The reduction of an iron oxide catalyst by the nitrogen-hydrogen mixture has been studied (Latschinov, J. Appl. Chem. Russia, 1937, 10, 1847; 1940, 14, 1260). The activity of an iron catalyst is impaired by lubricating oil (which may originate in gas compressors) (Kamzolkin and Livschitz, J. Chem. Ind. Russ. 1937, 10, 1225). The activity of a  $Fe_2O_3-Al_2O_3-K_2O$  catalyst is reduced by 25% by 0.001% of hydrogen sulphide at 500°, and at 450° 0.0001% of hydrogen sulphide reduces it by 70%; phosphine does not inactivate it at any temperature above 510° (Kamzolkin and Avdeeva, *ibid.* 1933, 10, No. 7, 32). The poisoning of a titanomagnetite catalyst reaches a maximum after an hour, then falling slightly to a constant value (Epschtein, *ibid.* 1933, 10, No. 2, 41). The poisoning effect of water vapour increases with pressure (Kamzolkin and Livschitz, *ibid.* 1937, 14, 244). A review of catalyst poisons is given by Pastonesi (Chim. e L'Ind. 1937, 19, 123).

Other proposed catalysts are carbonyl iron with promoters of  $Al_2O_3$ ,  $MgO$ , etc. (I.G. Farbenind. A.-G., B.P. 267554, 1926), ferrites (Collett, B.P. 237394, 1924), ferrocyanides and complex cyanides (Uhde, B.P. 273735, 1927; Hurter, B.P. 305753, 1927), catalysts with a zeolitic base (Selden Co., B.P. 307457, 1928), and iron with arsenic, phosphorus, or boron (Soc. Chem. Ind. Basle, B.P. 359378, 1930).

Hydrazine (up to 4% of nitrogen fixed at 437° with very high flow-rates) may be formed as well as ammonia with iron catalysts (Gedye and

Rideal, J.C.S. 1932, 1169). There may be some relation between the electron emission and activity of a catalyst (Kunsman, J. Physical Chem. 1926, 30, 525; J. Franklin Inst. 1927, 203, 635; J. Amer. Chem. Soc. 1929, 51, 688; Brewer, *ibid.* 1931, 53, 74).

The physical properties of nitrogen and hydrogen, and mixtures of them, and of gaseous and liquid ammonia, have been fully investigated (Larson and Dodge, *ibid.* 1923, 45, 2918; Osborne, Stimson, Sligh, and Cragoe, Bur. Stand. Bull., Washington, 1935, 20, 65, Sci. Paper No. 501; Verschoyle, Proc. Roy. Soc. 1926, A, 111, 552; Bartlett, J. Amer. Chem. Soc. 1927, 49, 687; 1928, 50, 1275; 1930, 52, 1363; Merz and Whittaker, *ibid.* 1928, 50, 1522; Beattie and Laurence, *ibid.* 1930, 52, 6; Deming and Shupe, *ibid.* 1930, 52, 1382; Beattie and Ikehara, Proc. Amer. Acad. Arts Sci. 1930, 64, 127; Mackay and Krase, Ind. Eng. Chem. 1930, 22, 1060; Keyes, J. Amer. Chem. Soc. 1931, 53, 965; Clifford and Hunter, J. Physical Chem. 1933, 37, 101 (system ammonia-water). The moisture content of compressed nitrogen (Bartlett, J. Amer. Chem. Soc. 1927, 49, 65; Walker and Ernst, Ind. Eng. Chem. [Anal.], 1930, 2, 139; Saddington and Krase, J. Amer. Chem. Soc. 1934, 56, 353), and the much enhanced vapour pressure of liquid ammonia in presence of compressed gas (Larson and Black, *ibid.* 1925, 47, 1015, 3107; Cupples, *ibid.* 1929, 51, 1026) have been investigated.

The reaction  $N_2 + 3H_2 = 2NH_3$  is exothermic; J. Thomsen ("Thermochemistry," Longmans, 1908, p. 245) gives 11,890 g.-cal. for the heat of formation of  $NH_3$  at 1 atm. pressure at 18°; Berthelot and Matignon give 12,200 g.-cal. at higher temperatures; Nernst (Z. Elektrochem. 1910, 16, 96) calculated 15,100 g.-cal. at 850°; Haber and Tamaru (*ibid.* 1915, 21, 191) and Haber, Tamaru, and Ohlm (*ibid.* p. 206) found results summarised below:

$t, ^\circ C.$	$Q_p$ obs. (kg.-cal.)	$Q_p$ calc. (kg.-cal.)
0	10.95	10.95
466	12.67	12.67
503	12.70	12.77
554	12.86	12.91
659	13.10	13.15

$$Q_p = 10,950 + 4.5t - 0.001822t^2 \text{ g.-cal.}$$

Haber and Tamaru (*ibid.* 1915, 21, 228) give for the true molecular heat of ammonia at constant pressure:

$$C_p = 8.62 + 0.0035t + 5.1 \times 10^{-6}t^2 \text{ g.-cal.}$$

Nernst's results (*ibid.* 1910, 16, 96) are somewhat lower:

$t, ^\circ C.$	$C_p$ obs. (H. and T.)	$C_p$ obs. (N.).
309	10.3	9.45
422	11.0	10.0
523	11.8	10.7

The values of the equilibrium constant

$$[NH_3]^2/[N_2][H_2]^3 = K$$

at various temperatures (Habor, *ibid.* 1914, 20, 597; Todd, in "Physical and Chemical Data of Nitrogen Fixation," Munitions Inventions Dept., Ministry of Munitions, H.M. Stationery Office, 1918; Maurer, Z. anorg. Chem. 1919, 108, 273; Claude, Compt. rend. 1919, 169, 1039; Todd, Proc. Durham Phil. Soc. 1920, 6, 1; Tour, Ind. Eng. Chem. 1921, 13, 298; Larsen and Dodge, J. Amer. Chem. Soc. 1923, 45, 2918; Larsen, *ibid.* 1924, 46, 367, 1002; Moldenhauer, Chem.-Ztg. 1925, 49, 65; Lurie and Gillospio, J. Amer. Chem. Soc. 1926, 48, 28; 1927, 49, 1146; Mittasch and Frankenburg, Z. Elektrochem. 1929, 35, 920; Besch, Chem. Fabr. 1933, 6, 127; Newton and Dodgo, Ind. Eng. Chem. 1935, 27, 577; Stephenson and McMahon, J. Amer. Chem. Soc. 1939, 61, 437) show a marked increase with pressure. The equilibrium percentage of ammonia in gas of composition  $N_2 + 3H_2$  is shown below.

Atm. (abs.).	10	50	100	300	600	1,000
350°C..	7.41	25.23	37.35	59.12	75.02	87.46
400°C..	3.85	15.27	25.12	47.00	65.20	79.82
500°C..	1.21	5.50	10.61	20.44	42.15	57.47
600°C..	0.49	2.25	4.52	13.77	23.10	31.43
700°C..	0.23	1.05	2.18	7.23	12.60	12.87

This table is based on experiments at 325–500°C. and pressures of 10–1,000 atm. (abs.) and the accuracy is within 2%. The yield falls off as the temperature rises, but at very high temperatures it appears to increase again (Maxted, J.C.S. 1918, 113, 168, 386; 1919, 115, 113; J.S.C.I. 1918, 37, 232r; B.P. 130023, 130063, 1919; Briner, Holv. Chim. Acta, 1919, 2, 162).

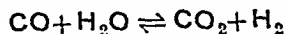
A sketch of the industrial synthesis of ammonia is given in the section on AMMONIA (Vol. I, 3356). A description of the plants at Oppau and Mersburg is given here (cf. Bosch, Industrial Chemist, 1934, 10, 90).

The two factories, besides providing ammonia, manufacture ammonium sulphate, chloride, carbonate, and nitrate; nitric acid, and sodium and potassium nitrates; urea; and various mixed fertilisers.

The power for both plants is produced from lignite, gasified in "Bamag" producers, 12 ft. by 25 ft., with rotary grates, a little steam being added to the air. In the Oppau works the power plant generates 15,000–16,000 h.p. A row of 12 gas producers, each consuming 20 tons of lignite and yielding 2,000,000 cu. ft. of gas per day, is built alongside a similar row of water-gas generators, which provide the hydrogen. The latter use Ruhr oven coko, and are of the Pintsch type with rotary grates, 15 ft. by 25 ft., gasifying over 30 tons of coko to 3,000,000 cu. ft. of gas each daily. Some air is added, and the resulting gas contains  $H_2$  40,  $CO$  30,  $CO_2$  12,  $N_2$  18%, approximately.

The water gas is treated to produce hydrogen by the Bosch process (B.P. 26770, 1912; 27117, 1912; 124760, 1917; U.S.P. 1115776, 1914; 1200805, 1916; Z. kompr. u. flüssige Gase, 1914, 16, 187; Tour, Chem. and Met. Eng. 1922, 26, 245, 307, 359, 411, 463; Taylor, *ibid.* 1922, 27, 1263; S. J. Green, "Industrial Catalysis,"

Benn, 1928, pp. 157 *et seq.*, 324 *et seq.*; Brownlie, Ind. Eng. Chem. 1938, 30, 1139). In this a mixture of water gas and steam is passed over a catalyst consisting of ferrio oxide with promoters such as chromium oxide at a temperature of 400–500°, when the reaction



takes place. The catalyst remains active for two years. The catalyst plant comprises 24 units in two sections of two rows of six or seven units. Each unit has two heat exchangers and one elevated catalyst chamber; the latter is 16 ft. by 12 ft. by 10 ft. deep, with an oval cover carrying two 8-in. pipes, and contains two trays of catalyst. The heat exchangers are 30 ft. by 15 ft. by 6 ft., and the whole apparatus is lagged, so that the reaction takes place without external heating. (The addition of a little oxygen or air to the gas has been described as a means of maintaining the temperature, a free flame burning in the catalyst chamber.) The gas issuing from the hydrogen converters (in which the reaction is conducted at atmospheric pressure) contains a little carbon monoxide (according to H. C. Greenwood, "Industrial Gases," Baillière, 1920, p. 163, this may be 2.5%) and must be purified from carbon dioxide, residual carbon monoxide, and hydrogen sulphide (from sulphur in the coko).

The purification (B.P. 9271, 1914; 120516, 1917; F.P. 389671, 1908; U.S.P. 1196101, 1916) is carried out by first washing out the carbon dioxide with water under pressure (B.P. 11878, 1910; 124761, 1917); washing finally with soda (B.P. 15053, 1914) is not used. Carbon monoxide is then taken out by washing with ammoniacal cuprous formate solution, followed by hot sodium hydroxide solution, both under high pressure (B.P. 1759, 1912; U.S.P. 1126371, 1915; 1133087, 1915; J. Amer. Chem. Soc. 1921, 43, 1). The hydrogen sulphide is also removed. The copper solution contains excess of ammonia (not less than 6%) to prevent iron being attacked; the alkali solution may contain 25%  $NaOH$ , and is brought in contact with the gas at 260° under 200 atm. In modern plants the alkali wash is not used.

In the purification from carbon dioxide the gas, carried by a 3-ft. main from the converters, is compressed to 25 atm. and passed to the bases of eight steel towers, 30 ft. by 4 ft., packed with rings, into the tops of which water at 25 atm. pressure is injected by circulating pumps. The water issues charged with carbon dioxide; it is passed through Pelton wheels, in which 60% of the power is recovered, and the carbon dioxide evolved is collected. It is more than sufficient to convert all the ammonia made into ammonium sulphate by the gypsum process, or into chloride by the ammonia-soda process. The gas is now passed through steel bottles, which act as spray catchers, to the high-pressure plant. Here it is brought to 200 atm. and delivered to the purifiers which remove carbon monoxide.

This plant consists of 16 towers of special steel, each in one piece, 25–30 ft. high and 2 ft. 6 in. in external diameter, with flanged ends, and packed with Guttman balls. In the first eight of these, ammoniacal cuprous formate solution

(cf. Richardson, U.S.P. 1962525, 1934) is circulated, in the remainder sodium hydroxide ( $\text{CO} + \text{NaOH} = \text{H} \cdot \text{COONa}$ ). The liquids are circulated by eight hydraulic pumps of forged steel, 200 h.p. total, and the ammoniacal copper solution, which absorbs ten times its volume of carbon monoxide, is passed down a 40-ft. tower, when the gas is released and collected. Spray traps in the form of vertical steel bottles are placed under these towers. The presence of 0.01% of carbon monoxide in the final gas is said to be injurious.

A solution of cuprous chloride in hydrochloric acid is said to be better than an ammoniacal solution for normal carbon monoxide absorption (Pyke, J. Proc. Austral. Chem. Inst. 1938, 5, 201), but under high-pressure conditions this is uncertain. The ammoniacal cuprous solution may be regenerated by heating slowly to 50°, allowing oxygen to combine with carbon monoxide, expelling the carbon dioxide, and then removing the residual monoxide by heating rapidly to 70–80° (Chemical Construction Corp., U.S.P. 2047550, 1936).

The purified hydrogen (with some nitrogen from the air mixed in the water-gas operation) is now passed to the catalyst plant by a high-pressure main. The nitrogen content is brought up to the ratio  $\text{N}_2:3\text{H}_2$  from a Linde plant and the gas is dried. This is the optimum ratio, the presence of argon being deleterious, but not seriously so, at all pressures (Gillespie and Beattie, J. Amer. Chem. Soc. 1930, 52, 4239; Pavlov and Gaurilov, J. Chem. Ind. Moscow, 1933, 10, No. 3, 22; Toniolo and Giamarco, Giorn. Chim. Ind. Appl. 1933, 15, 219).

The catalyst plant in which the mixture is converted into ammonia consists of 15 steel converters, each comprising two straight flanged sections, each 6 m. long and 80 cm. in internal diameter, the walls being 18 cm. thick. These are bolted together and the covers are held on by fifteen 4-in. studs. The walls are perforated at intervals of 1 ft. with  $\frac{1}{4}$ -in. tapering holes for the purpose of releasing any gas which leaks behind the liners. Inside is a special steel liner, making a gas-tight joint with the ends (U.S.P. 1188530, 1916; G.P. 254571 and 256296, 1911) to prevent attack of the carbon-steel retaining wall by the hydrogen; a lining of electrolytic iron might be possible. Inside this liner is probably a refractory lagging and a support for the catalyst, the internal diameter of the catalyst space being 50 cm. The outer walls are heavily lagged, and reach 300–400°; the catalyst is at 600°. (In some other installations the outer walls are not lagged, but are exposed to the air.) The temperature is maintained by heat exchangers (Nitzschmann, Chem. Listy, 1928, 22, 169, 199, 241), consisting of forged steel tubes, 6 m. long and 15 in. in external diameter, fitted internally with nests of  $\frac{5}{8}$ -in. steel tubes autogenously welded into end plates. Each catalyst unit is mounted vertically with its heat exchanger inside a brickwork compartment with strong iron doors and planking, with a little of the bomb projecting above. (In some works the row of catalyst units is built against a strong wall, the exposed units being unprotected.) Starting may be effected by adding

oxygen (which does not come into contact with the catalyst) (G.P. 259870, 1911) or by electrical heating (U.S.P. 1202995, 1916). An iron catalyst with a promoter is used. The converter has a long life (twenty years) (Edwards, Chem. Met. Eng. 1939, 46, 361).

The gas is circulated through the catalyst; argon and methane (from residual carbon monoxide) may accumulate up to several per cent. and must be blown off periodically along with some  $\text{N}_2 + 3\text{H}_2$  mixture; 10% of the gas is lost by leakage.

The ammonia is removed from the gas by solution in water under pressure (G.P. 235421, 1908; 270192, 1912); liquefaction (U.S.P. 1202995, 1916) is not economical with the percentage of ammonia obtained in the gas by the Badische process, but is possible with the Claude process (p. 550*d*), when the gas is richer in ammonia. Three water injector pumps are connected with nine sets of absorbers, each consisting of three water-cooled steel spirals set vertically, the upper spiral being 60 ft. above ground. The gas passes down the lowest spiral, rises to the top of the second spiral and passes down this, and similarly with the third spiral. Water flows down all the spirals by gravity. A solution containing 25% of ammonia is obtained. The unconverted gas is dried and sent back to the catalyst system.

The fuel requirements at Oppau (McConnell, Ind. Eng. Chem. 1919, 11, 837) were 1,750 tons of lignite (400 for gas engines, 1,000 for steam for hydrogen plant, and 350 for power plant), and 500 tons of coke (for hydrogen) per day. The daily cost of labour was £2,300, of fuel £2,300, and working expenses, interest, etc., £6,700.

The process at Merseburg differs from that at Oppau in two respects and represents a more modern practice: (1) the mixture of nitrogen and hydrogen is made directly by treating a mixture of producer (air) gas and water gas, with the addition of steam, by the Bosch process (Van der Werth, Chem. Ztg. 1935, 59, 276); (2) the purified mixture of nitrogen and hydrogen, before passing to the main catalyst, is passed through a series of small catalyst vessels ("Vorofen") to remove impurities (B.P. 5835, 1911).

At Merseburg there are 31 gas generators, five for air gas and the rest for water gas, all the air being provided by two blowers, each of 350 h.p. The gases pass through three gas-holders, each of 1,765,000 cu. ft. capacity, providing a reserve for 15 minutes. From these they are taken and mixed by blowers. The mixed gas then takes up the requisite amount of water vapour in two rows of six towers, each 82 ft. high, through which hot water is pumped by seven pumps, each of 70 h.p. The water is warmed in a tower by the gas leaving the heat exchanger of the contact converters for the hydrogen production. There are 48 heat exchanger towers.

The gas, containing hydrogen, nitrogen, carbon monoxide, steam, and some carbon dioxide, passes, after preheating, to two sets of 24 contact furnaces in which the reaction



occurs. The gas then passes to two gas-holders,

one of 350,000 cu. ft. and the other of 1,050,000 cu. ft. capacity. Carbon dioxide is removed by washing in 21 to 30 towers at 25 atm., the compression of the gas being in large part effected by one of the cylinders of the 200 atm. compressors, although a few pumps for 25 atm. are provided. Pelton wheels recover about 40% of the energy of the released gas, which is utilised to compress the water to 25 atm. The power for this part of the plant is 40,000 h.p. (Schneider, Brennstoff-Chem. 1931, 12, 273; Anon. J.S.C.I. 1929, 48, 591; Chem.-Ztg. 1930, 54, 2, 29, 66; Waeser, Chem. Fabr. 1932, 5, 248, 266, 273).

For the removal of the carbon monoxide, the gas compressed to 200 atm. by twenty-four 1,000 h.p. compressors and twelve 500 h.p. compressors (for a study of the nitrogen-hydrogen-carbon monoxide mixture, see Vorschöyle, Phil. Trans. 1931, 230, 189) is scrubbed in 19 towers with ammoniacal cuprous formate solution circulated by nine double pumps of 600 h.p. The carbon monoxide recovered by reducing the pressure in towers is sent to the hydrogen contact plants. Six towers for sodium hydroxide solution remove the remaining carbon monoxide, this solution being circulated by six small pumps.

The gas now passes to nine small contact furnaces ("Voröfen"), in which the remaining impurities are removed by the catalyst mass before passing to the main contact system. There are 24 main catalyst units (five being in reserve), and 24 heat exchangers. Circulation is effected by 11 pumps of 700 h.p. each. The ammonia formed is absorbed in water compressed to 200 atm. by five 100 h.p. and two 300 h.p. pumps, in 20 towers 39.3 ft. high and 29 in. in diameter. The ammonia solution is passed to an expander, the ammonia gas evolved being absorbed in a separate tower. In the expansion the hydrogen and nitrogen gases dissolved in the water under 200 atm. pressure are liberated; these pass through the ammonia scrubbing tower and are collected in a gas-holder, from which they re-enter the circulatory system.

Absorption of ammonia from the gas by moist silica gel or active alumina, regenerated by steam or dry ammonia-free gas, is proposed (I.G.-Farbenind., B.P. 495026, 1937; not granted).

The synthetic ammonia factory of Imperial Chemical Industries at Billingham uses a process similar to that used at Merseburg (Pollitt, J.S.C.I. 1927, 46, 291r) with a production in 1931 of 150,000 tons of ammonia, and another works under their control is operating at Moddersfontein in South Africa (South African Min. and Eng. J. 1931, 42, 3, 39; Trans. South African Inst. Elec. Eng. 1932, 23, 265).

The deterioration of steels under the action of the compressed heated mixture containing hydrogen, nitrogen, and ammonia is important. Ordinary carbon steels are quickly penetrated and fissured by the carbon dissolving to form methane, and all steels are attacked to some extent and their tensile strength lowered. Nickel steels are deeply penetrated but show a high residual strength; chromium steels deteriorate more rapidly as the carbon content

increases; addition of molybdenum and nickel improves their resistance. High-chromium and nickel-chromium steels of the stainless type are best, but are difficult to forge and machine. Vanadium produces an appreciable improvement (Thompson, Trans. Amer. Electrochem. Soc. 1926, 50, 101; Vanick, Trans. Amer. Soc. Steel Treat. 1927, 12, 169; Vanick, de Sveshnikoff, and Thompson, U.S. Bur. Stand. Tech. Paper, No. 361, 1927, 22, 199; Hadfield, J.S.C.I. 1930, 49, 48r; Inglis and Andrews, Engineering, 1933, 136, 613). According to Becket (J.S.C.I. 1932, 51, 52r), 2% of chromium limits penetration and fissuring of steel in ammonia converters to a minute depth, since the chromium nitride seals incipient fissures. Steels for such converters are specified to contain 1.5-2.25% of chromium and not over 0.30% of carbon; in some cases about 0.20% of vanadium is added. Molecular nitrogen is appreciably absorbed by iron only above 900°, the amount taken up being proportional to  $\sqrt{p}$  (Martin, Stahl und Eisen, 1929, 49, 1861; Sieverts and Krüll, Ber. 1930, 63 [B], 1071; Gray and Thompson, J.S.C.I. 1931, 50, 353r; Gray, *ibid.* 1932, 51, 537; Emmett and Brunauer, J. Amer. Chem. Soc. 1933, 55, 1738). Lining the converter with silicon or silicon alloys has been proposed (I.G. Farbenind.). An advantage of the Mont Cenis process (*q.v.*) is that, on account of the low working-temperature (370°), ordinary carbon steels may be used (Riley and Bott, Chem. Age, 1931, 24, 188). A copper-manganese alloy resists hydrogen and carbon monoxide at high temperatures (Bosch, Chem. Fabr. 1934, 7, 1).

Great numbers of methods of purifying the  $N_2+3H_2$  gas mixture before conversion have been described and patented (B. Waeser, "Die Stickstoffindustrie," Leipzig, 1924, p. 83; Müller, in Ullmann, "Enzyklopädie der technischen Chemie," 2nd ed., Vol. I, p. 349; A. Bräuer and J. D'Ans, "Fortsschritte in der anorg.-chem. Industrie an Hand der deutschen Reichspatente," Berlin, Band 1, 3 parts, 1921-23; Band 2, 2 parts, 1925; Band 3, 4 parts, 1928-30; Band 4, 3 parts, 1934-35; G. Schuchardt, "Technische Gewinnung von Stickstoff, Ammoniak, etc.," Sammlung chem. u. chem.-techn. Vorträge, 1910, 25, 213; L'Air Liquide, U.S.P. 1915723, 1933). These include scrubbing the gas with liquid ammonia, or with a solution of sodium in liquid ammonia, under pressure (Norsk Hydro.); the addition of a regulated amount of ammonia to the gas, say in the form of gas from the converters, followed by cooling to liquefy out the ammonia and impurities (Park, Slado, and Synthotic Ammonia and Nitrates, Ltd., B.P. 240350, 1925).

When the hydrogen is obtained from water gas it is usual (as at Merseburg) to blend the water gas and producer gas to form a mixture of carbon dioxide, carbon monoxide, hydrogen, and nitrogen, so that after separation of carbon dioxide, and the catalytic formation of hydrogen from admixed steam and the carbon monoxide (economy in which may be effected by using hot water-gas without condensation), a mixture of  $N_2+3H_2$  is obtained directly. Large numbers of methods for particular ways of producing



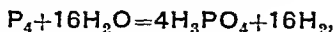
these mixtures are patented. I.G. Farbenind. (U.S.P. 1666694, 1928) pass through one producer steam and two mixtures of oxygen and nitrogen from air liquefaction, one richer and the other poorer in oxygen than atmospheric air, so that the resulting gas contains 1 vol.  $N_2$  to 3 vol. ( $H_2 + CO$ ). The removal of carbon monoxide from the gas by catalytic conversion to methanol has been proposed (Jordan, Proc. World Eng. Congr. 1929, 31, 139; Williams and Lazote Inc., B.P. 258887, 1925). In separating residual carbon monoxide the washing with ammoniacal copper solution, which may be cooled at  $0^\circ$ , alone is often used, the sodium-hydroxide pressure-wash being omitted (Dely and Synthetic Ammonia and Nitrates, Ltd., B.P. 220651, 1923; Chem. Trade J. 1931, 89, 471). Claude (Compt. rend. 1921, 173, 653; Ind. Eng. Chem. 1922, 14, 791) obtained hydrogen from water gas by liquefaction of the carbon monoxide. In Germany the I.G. Farbenindustrie makes cheap hydrogen from lignite, which can be steamed in powder form in a special type of gas producer.

The possibility of the conversion of methane in natural gas, coal gas, and gases from petroleum treatment, into hydrogen has received attention. Treatment with steam is one process (Armstrong, Chem. Trade J. 1931, 39, 448; J.S.C.I. 1930, 49, 53r). The Kuhlmann Co. in France convert methane in purified coke-oven gas into carbon monoxide by mixing with steam and heating at  $1,200^\circ$  in contact with a refractory containing over 75% of alumina, m.p.  $1,900^\circ$ , no specific catalyst being necessary (Chem. Trade J. 1931, 89, 453; Wietzel and Schiller, U.S.P. 1921856, 1933; Wilcox, U.S.P. 1901136, 1903845, 1905326, 1933; 1962418, 1934; Williams, U.S.P. 1938202, 1933; v. HYDROGEN, Vol. VI, p. 328).

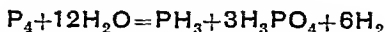
At Ougrée (Belgium) synthetic methyl alcohol is made as a preliminary to ammonia synthesis and very pure hydrogen is not necessary (Claude, Chim. et Ind. 1937, 37, 3). The methane content of coke-oven gas may be reduced from 21 to 0.5% by reaction with steam in presence of a nickel catalyst (Thau, Z. Ver. deut. Ing. 1938, 82, 862; cf. Du Pont de Nemours, U.S.P. 2064867, 1936; 2119565-6, 1938).

Explosion of methane-air mixtures gives a nitrogen-hydrogen mixture (Kabozev, Kazarovskii, and Kashtanov, J. Chem. Ind. Russ. 1935, 12, 1030).

In the Liljenroth process used at Merseburg, phosphorus vapour mixed with steam is passed over a catalyst at  $700$ – $1,000^\circ$  to produce hydrogen for ammonia synthesis and phosphoric acid for mixed fertilisers:



but the formation of phosphine:



is difficult to avoid (F. A. Ernst, "Fixation of Atmospheric Nitrogen," New York, 1928, p. 68; Wietzel and Pauckner, U.S.P. 1916594, 1933).

The use of sulphur instead of phosphorus is proposed (Norsk Hydro., B.P. 176779, 181326, 1921).

Coke-oven gas as a source of hydrogen was proposed by Claude (B.P. 130358, 1917; Compt. rend. 1919, 169, 649, 1039; 1920, 170,

174; 1921, 172, 974; 1922, 174, 157, 681; 1926, 182, 877; Ind. Eng. Chem. 1922, 14, 1118; Chim. et Ind. 1924, 11, 1055; 1937, 37, 3; Brownlie, Ind. Eng. Chem. 1938, 30, 1139; Cicali, U.S.P. 1885059, 1932).

In the original proposal, washing with a solvent such as ether at  $-50^\circ$  and 100 atm. pressure, was used, but in later processes purifying aqueous washes are used, followed by progressive cooling to liquefy all gases except hydrogen, washing with liquid nitrogen and addition of further nitrogen being used at the end to obtain the  $N_2 + 3H_2$  mixture. A recovery of 92% of the hydrogen in the coke-oven gas, with less than 0.02% of carbon monoxide, is claimed. In certain circumstances the process is more economical than that starting with water gas (Claude, Chem. Met. Eng. 1923, 28, 498; Moldenhauer, Chem.-Ztg. 1924, 48, 233; Anon., Metallbörse, 1924, 14, 817, 993; Z. angew. Chem. 1924, 37, 76; Schönfelder, Ber. Ges. Kohlentechn. 1925, 1, 397; Dodge, Chem. Met. Eng. 1926, 33, 416; Müller, Stahl und Eisen, 1928, 48, 405; Jordan, Proc. World Eng. Congr. 1929, 31, 139; Thau, Das Gas u. Wasserfach, 1930, 73, 767; Gas J. 1930, 191, 524; Pollitt, Trans. Sec. World Power Conference, Berlin, 1930, 2, 145; Armstrong, J. Soc. Arts, 1932, 80, 611).

Parrish (Chem. Age, 1933, 29, 591) gives per metric ton of ammonia as 25% liquor from coke-oven gas £6, water gas £7.2, electrolytic hydrogen £7 to £11.7, with power at 0.05d. to 0.15d. per kw.-hr.

In the *Casale* plant at Ostend (Pallemaerts, Ind. Eng. Chem. 1929, 21, 22) using the Union Chimique Belge method, the coke-oven gas is washed successively with ammonia solution, water, dilute sulphuric acid, and soda; it is then compressed to 9 atm., and washed with water to remove acetylene, cooled to  $-45^\circ$ , and fractionated by further cooling to separate ethylene, methane, and carbon monoxide in turn, the final gas being scrubbed with liquid nitrogen, further nitrogen gas being added to make up the mixture for synthesis.

In the *Mont Cenis* process the purified coke-oven gas is washed with liquid nitrogen in a Linde-Bronn separator, which takes out practically everything except hydrogen and nitrogen, is mixed with further nitrogen and then, containing 0.05% each of carbon monoxide and oxygen, is compressed to 100 atm., heated to  $300^\circ$  by interchangers, and passed over a nickel catalyst, which converts the carbon monoxide into methane and the oxygen into water. It is cooled to deposit part of the water, mixed with some gas from the ammonia converters, and cooled to  $-55^\circ$  to deposit liquid ammonia and impurities. The residual gas, containing 0.2–0.5% of ammonia, is heated in exchangers to  $320^\circ$  and then goes to the converters at  $370^\circ$ , the issuing gas containing 12–13% of ammonia.

The *Claude Process*.—Claude (B.P. 130086, 1917; 140083, 140089, 1918; 150744, 153254, 1919; J.S.C.I. 1921, 40, 420r; Scott, Colliery Guardian, 1924, 127, 737; Rugarcia, Rev. ing. ind. Madrid, 1932, 3, 321, 362) uses much higher pressures (up to 1,000 atm.) than in the Haber process. The increased cost of com-



pression from 250 atm. to 1,000 atm. is only one-third. The converters are much smaller, there is an increased evolution of heat which must be removed, and the gas is not recirculated, but passes back to the gasholders. The yield is 6 kg. of ammonia per kg. of catalyst per hour, as compared with 400 g. in the Haber process. The working temperature of the catalyst is 500–650°. The gas is so rich in ammonia (over 20% by vol.) that this can be liquefied under the high pressure by external water cooling, and the cold produced by the evaporation of the liquid utilised (on the solubility of hydrogen in liquid ammonia, see Wiebe and Gaddy, *J. Amer. Chem. Soc.* 1937, 59, 1984). The process may be combined with the Schreibe modification of the ammonia-soda process (G.P. 36093, 1885) to make ammonium chloride, or the ammonia can be converted into sulphate.

The catalyst tubes for the Claude process, which must withstand high pressure, may be cast solid and bored out from special nickel-chrome steel ("Viconic") not attacked by hydrogen. The heads fit with a gun-breech mechanism and copper washer. Four catalyst tubes form a unit, the first pair in parallel, the others in series. The tubes are 2 m. high and 100 mm. in outside diameter. The overall energy consumption is below 2.5 kw.-hr. per kg. of anhydrous ammonia. The life of the catalyst is 300 hours (*Z. angew. Chem.* 1930, 43, 417; Maxted, *Proc. Chem. Eng. Group Soc. Chem. Ind.* 1928, 8, 19). The Claude process is worked at Bethune and Waziers in France, in Belgium, Germany, Spain, America, and Japan.

At the Du Pont works at Belle, W. Va., the gas for conversion is compressed to 1,000 atm. in stages of 25, 85, and 320 atm., and the CO removed by conversion to methanol (Anon., *Ind. Eng. Chem.* 1930, 22, 433).

**The Casale Process.**—This process (Braham, *J. Ind. Eng. Chem.* 1922, 14, 791; J. R. Partington, "The Alkali Industry," Baillière, 1925, p. 263, Fig. 73), first operated in Italy, resembles the Claude in using a high pressure (600–900 atm.), but regulates the production of heat in the converter by leaving a proportion of ammonia in the gas recirculated. The working temperature is about 500°C., with a space-time velocity (cu. ft. gas at S.T.P. per hour per cu. ft. catalyst) of 12,000. The effluent gas contains 15% of ammonia. The catalyst is made by burning iron in oxygen under high pressure so as to oxidise 5–15% and volatilise harmful impurities. The converter is 20 ft. long and 14 in. in internal diameter, and contains about 10 cu. ft. of catalyst disposed in an annular ring 3 in. thick and 18 ft. long. The entering gas passes up in contact with the inner surface of the shell, in heat-exchange contact with the hot exit-gas. It then passes down an electric heater in the core of the shell, the whole process being kept slightly endothermic, up through the annular catalyst, down the heat exchanger, and out. The catalyst is changed every year. The process is used at Terni (Rome), Ostend (750 atm.), Toulouse (the largest French factory), Niagara Falls, Japan, etc. (*Ind. Eng. Chem.* 1929, 21, 22). The Casale plant in Canada, at Sandwich, which supplied all the anhydrous ammonia required in the

Dominion, prepares the mixed gas by burning electrolytic hydrogen in air so as to give directly  $3\text{H}_2 + \text{N}_2$ , which is scrubbed and converted (Brown, *Chim. et Ind.* 1934, 32, 759). Part of the ammonia is oxidised to nitric acid at Beloeil, Quebec (*Chem. Age*, 1931, 25, 6).

**The Fauser Process.**—This was introduced by the Società Elettrochimica Novareso at Novara, Italy (*J.S.C.I.* 1923, 42, 835n; Fauser, *Giorn. Chim. Ind. Appl.* 1931, 13, 361; I progressi dell' industr. chim. ital., Assoc. Ital. di Chimica, Rome, 1932, 55; Congr. int. Quim. pura appl. 1934, 9, III, 402; Pastonesi, *Industria Chimica*, 1932, 7, 583; *Chim. e L'Ind.* 1936, 18, 511; *Chim. et Ind.* 1937, 35, 1115; *Giorn. Chim. Ind. Appl.* 1934, 14, 444, 615; Zambianelli, *Chem. Age*, N.Y., 1923, 31, 413; Bräuer, Reitschötter, and Siebenreicher, *Angew. Chem.* 1933, 46, 7; Maveri, *Chim. e L'Ind.* 1939, 21, 572). It works at a moderate pressure of 250–300, or even 200 atm., the gases being preheated to 600° in a battery of tubes embedded in the catalyst material, and the temperature is gradually lowered to 450° as the proportion of ammonia increases. Ammonia not liquefied by cooling is dissolved out in water used to lubricate the compressor, and the dissolved gas is driven out in a heat exchanger warmed by the converter gas.

The Fauser plant of the Consolidated Mining and Smelting Co. at Trail, B.C., with a capacity of 47 tons of ammonia per day, uses electrolytic hydrogen, and nitrogen from a Claude plant. The operating pressure is 300 atm., liquid ammonia being obtained directly, and stored in a 30-ft. diameter Horton sphere (McMichael, *Chem. Met. Eng.* 1930, 37, 484; *J.S.C.I.* 1931, 50, 625n; *Chem. Trade J.* 1931, 89, 524; Kirkpatrick, *Chem. Met. Eng.* 1931, 38, 626; *Ind. Eng. Chem.* 1930, 22, 433, for transport of ammonia).

The largest Fauser installation (40,000 tons of nitrogen per annum) is at Sluiskil, Holland, operated by the Compagnie Néerlandaise de l'Azote (Borelli, *Chem. Met. Eng.* 1932, 39, 126; *Chem. Age*, 1932, 26, 368; *Chem. Trade J.* 1933, 92, 464). Both coke-oven gas and water gas are used, the pressure in the converter being 250–300 kg. per sq. cm. and the total capacity of the six converters is 600 tons of ammonia per 24 hours. An activated iron catalyst is used, which requires renewal once a year. Two preliminary converters transform any residual carbon monoxide into methane, which is not a catalyst poison. Preliminary heating is electrical, but once reaction has started the current is shut off. Ammonium sulphate is produced at Sluiskil (Fauser, B.P. 292129, 1927) in a steel reaction chamber in which ammonia gas is introduced at the bottom and meets a shower of sulphuric acid distributed at the top. The heat of reaction volatilises the water and the dry salt is removed from the bottom by screw conveyers. The plant can produce 800 tons per 24 hours.

Fauser plants are in operation in other parts of Holland, in Germany (Piesteritz), Poland (Tarnow), Sweden, Japan, etc.

**The Duparc Process.**—This process (B.P. 140061, 1919; Duparc, Wenger, and Urfor, *Holv. Chim. Acta*, 1930, 13, 650) was to work at

atmospheric pressure and 325° to produce a gas containing 25% of ammonia, but does not seem to have been used technically.

**The Mont Cenis Process.**—This was set in operation near Essen in Germany in 1928, producing 24,000 tons of fixed nitrogen per year. There are plants also in Holland, France, and America. A low pressure of 98 atm. and a low temperature of 400°C. are used. With a practical speed of working, the effluent gas contains 20% of ammonia. The special features are the catalyst (Uhde, B.P. 273735, 1926) and the purification of the gases (Scholvien, Chem. and Met. Eng. 1931, 38, 82; Chem. Age, 1931, 24, 304; Parrish, *ibid.* 1931, 25, 581; Armstrong, J. Soc. Arts, 1932, 80, 611).

Synthetic ammonia plants using coke-oven gas (probably Mont Cenis or modified processes) in use in Germany in 1932 (Ullmann, "Enzyklopädie der technischen Chemie." Vol. IX, p. 720) with the stated capacities in metric tons of fixed nitrogen per annum were: Mont Cenis (30,000), Herne (40,000), Holten-Sterkade (45,000), Scholwen (52,000; Mont Cenis, making liquid ammonia), Ost-Erkenschwick (22,500) Waldenburg (22,500), and Rexel (20,000; Claude, making liquid ammonia).

The American synthetic ammonia production for 1931 was estimated at 290,000 tons (Riley and Bott, Chem. Age, 1931, 24, 188). The synthetic plants in America, in order of capacity, are: Atmospheric Nitrogen Corporation, Syracuse, N.Y.; Lazote Inc. (Du Pont Subsidiary) at Charleston, W. Va.; Mathieson Alkali Works, Niagara Falls (using electrolytic hydrogen); Niagara Ammonia Co. (Du Pont Subsidiary); Roessler-Hasslacher Chemical Co., Niagara Falls; the Pacific Nitrogen Corporation (Du Pont Subsidiary) at Seattle, Washington; the Great Western Electrochemical Co. at Pittsburg, Calif. Of the American plants, calculated on capacity, 57% operate with water gas, 32% on by-product hydrogen, and 11% on electrolytic hydrogen. Synthetic sodium nitrate is made at the Hopewell, W. Va., works (Chem. Trade J. 1931, 88, 388).

The world capacity of synthetic ammonia plants in 1936 was given as 6,600,000 tons of ammonia per annum (Breslauer, Chem. Met. Eng. 1936, 43, 282).

Ammonia gas is catalytically decomposed in contact with heated metals such as iron, platinum, and tungsten (Perman and Atkinson, Proc. Roy. Soc. 1904, 74, 110; Bodenstein and Kranendieck, Nernst Festschrift, 1912, 99; J.C.S. 1912, 102, ii, 1155). On platinum and tungsten the rate of decomposition at a given temperature is given by

$$-dc/dt = k_c / (\delta n + \epsilon h)$$

where  $c$ =ammonia pressure,  $n$ =nitrogen pressure,  $h$ =hydrogen pressure, and  $k$ ,  $\delta$ , and  $\epsilon$  are constants (Hinshelwood and Burk, *ibid.* 1925, 127, 1105; Schwab, Z. physikal. Chem. 1927, 128, 161; 1928, 131, 446).

The use of "cracked" synthetic ammonia ( $N_2 + 3H_2$ ) or ammonia itself for heat-treatment of metals, etc., has been proposed (Anon., Ind. Eng. Chem. 1930, 22, 433; Pollitt, Chem. Age, 1931, 25, 570; Burke, U.S.P. 1915120, 1933;

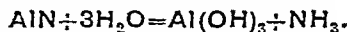
Hall and Imp. Chem. Ind., B.P. 380110, 1931; Chem. Trade J. 1931, 89, 206; 1933, 92, 459; Brandt, Metals and Alloys, 1942, 16, 60).

#### FIXATION OF NITROGEN AS NITRIDES.

Many elements, such as lithium, calcium, magnesium, and boron absorb nitrogen when heated, forming nitrides which are decomposed by water with evolution of ammonia (E. B. Maxted, "Ammonia and the Nitrides," Churchill, 1921; Franck, Bredig, and Hoffmann, Naturwiss. 1933, 21, 330). A more promising reaction is the formation of aluminium nitride  $AlN$  from nitrogen and a mixture of alumina and carbon at very high temperatures:



Aluminium itself begins to absorb nitrogen at 750° (Fichter and Oesterheld, Z. Elektrochem. 1915, 21, 50). Aluminium nitride can be decomposed by heating with water and a little alkali under pressure, with production of alumina, which may serve for the manufacture of metallic aluminium:



These reactions were applied in the Serpek Process (B.P. 13086, 1910, and numerous later patents; summary in Gmelin, "Handbuch der anorganischen Chemie," Berlin, 1933, Part, 35b, p. 137), which was worked for a time in the Savoy, but later abandoned. The absorption is greatly accelerated by iron oxide, so that bauxite forms a suitable raw material. A temperature of 1,800°C. was necessary, the time of contact was 5-6 hours, and the refractories suffered considerably. The original claim was 1 kg. of nitrogen fixed for 10-12 kw.-hr.

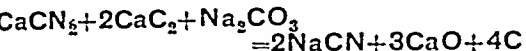
Serpek states that a mixture of hydrogen and nitrogen gives better results than producer gas. The Shoeld furnace is similar to that used for cyanamide (p. 554b), with a central heating rod of carbon, the charge being a briquetted mixture of 3 parts of alumina and 1 part of carbon. In the latest type of furnace proposed (Z. komprimierte u. flüss. Gase, 1914, 16, 55) a short chamber, 4 m. high and 1.5 m. wide, is used. The mixture of bauxite and carbon is dropped through the nitrogen at a temperature not exceeding 1,250-1,300°, and conversion takes place more rapidly than in the old type of revolving furnace; producer gas is used, and pure carbon monoxide passes out of the furnace. Two tons of alumina are obtained and 500 kg. of nitrogen fixed per h.p.-year. The process does not appear to be used on the industrial scale. (See also Richards, J. I. & L. Chem. 1913, 5, 335; Tucker, J.S.C.I. 1913, 32, 1143; Escher, Chem.-Ztg. 1918, 42, 353, 361; Shoeld, U.S.P. 1344153, 1920; Herman, G.P. 319046, 1920; Krauss, Thompson, and Yee, Ind. Eng. Chem. 1926, 18, 1287).

#### FIXATION OF NITROGEN AS CYANIDES.

The production of alkali and alkaline-earth cyanides starting with elementary nitrogen, and the hydrolysis of the cyanides with formation of ammonia, has often been proposed, and at

one time the Bucher process (J. Ind. Eng. Chem. 1917, 9, 233; *v.* CYANIDES, Vol. III, 482) attracted some attention. It has never been of any significance as a source of ammonia, and later developments have been concerned with attempts to produce cyanides (*see* Heise and Foote, *ibid.* 1920, 12, 331; Monnt, *Met. Chem. Eng.* 1920, 22, 709; Thompson, *ibid.* 1922, 26, 124; Berl and Braune, *Fortschr. Chem. Phys. n. phys. Chem.* 1925, 18, 199; Guernsey *et al.*, *Ind. Eng. Chem.* 1926, 18, 243).

The Thann process for the production of sodium cyanide depends on the reaction



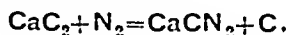
Hatt, *Chim. et Ind.* 1932, 28, 777; *cf.* Kretov, *J. Chem. Ind. Moscow*, 1933, 10, No. 4, 28; Carlisle, *Ind. Eng. Chem.* 1933, 25, 959; Buchanan, *Chim. et Ind.* 1932, 28, 1024; Bräner, Reitstötter, and Siebenreicher, *Angew. Chem.* 1933, 46, 7). The reduction of sodium cyanate to cyanide by carbon monoxide is practically quantitative at 700° (Drucker and Henglein, *Z. physikal. Chem. Bodenstein Festb.* 1931, 437).

The synthesis of hydrocyanic acid from nitrogen and hydrocarbons (*v.* CYANIDES, Vol. III, 498b) has been studied.

#### THE CYANAMIDE PROCESS.

(*See also* Vol. II, 219c.)

According to Moissan (*Compt. rend.* 1894, 118, 501) calcium carbide does not absorb nitrogen at 1,200°, but Rothé, and Frank and Caro (G.P. 92587, 1895; 227854, 1907; *Z. angew. Chem.* 1903, 16, 658, 753; 1906, 19, 835; 1909, 22, 1178), working with crude carbide, found that absorption occurs readily at that temperature, with the formation of a mixture of calcium cyanamide and graphite by an exothermic reaction:



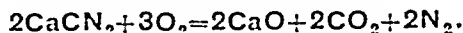
With barium carbide 30% of the nitrogen is absorbed as barium cyanide,  $\text{Ba}(\text{CN})_2$ , and the rest as barium cyanamide,  $\text{BaCN}_2$  (Erlwein, *Z. angew. Chem.* 1903, 16, 533; Askenasy, G.P. 382041, 1922; Deguide, F.P. 591019, 1924; Grude, *Z. Elektrochem.* 1922, 28, 150; Askenasy and Bring, *ibid.* 1926, 32, 216; Schweitzer, *ibid.* 1926, 32, 98). The yield of calcium cyanamide is about two-thirds of the theoretical.

The crude dark-grey product of the absorption of nitrogen by calcium carbide is known as "nitrolim" or "Kalkstickstoff" and contains about 20% of combined nitrogen. When treated with water to remove unchanged carbide the product is called "cyanamide" and is used as a fertiliser.

The absorption of nitrogen by carbide is reversible at 1,360° and the best temperature for the reaction is 1,000–1,100°.

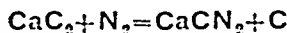
Finely powdered calcite heated in a mixture of ammonia (95%) and carbon dioxide (5%) at 800° gives a product containing 92–94% of  $\text{CaCN}_2$  (Nagai and Yamaguchi, *J. Soc. Chem.*

*Ind. Japan*, 1940, 43, 361b), and pure calcium cyanamide (which is white) is obtained by heating dicyanodiamido ( $\text{H}_2\text{CN}_2$ )<sub>2</sub> (*v.* Vol. III, 602d) with calcium oxide in nitrogen at 900–1,000° (Kameyama, *J. Coll. Eng. Tokyo*, 1920, 10, 173). It oxidises in air above 400°:



The crystal structure is analogous to that of sodium azide  $\text{NaN}_3$  with a hexagonal lattice (Bredig, *J. Amer. Chem. Soc.* 1942, 64, 1730).

The system:



was investigated by Bredig, Fraenkel, and Wilke (*Z. Elektrochem.* 1907, 13, 69, 605; *cf.* Foerster and Jacoby, *ibid.* 101; Rudolfi, *Z. anorg. Chem.* 1907, 54, 170), who found that the rate of absorption of nitrogen is proportional to the pressure, other things being constant. Thompson and Lombard (*Met. Chem. Eng.* 1910, 8, 617, 682) found that the system is univariant, there being a fixed equilibrium pressure of nitrogen at each temperature. The pressure-temperature curve has two branches, the branch from 910°C. to 1,150°C. rising like a vapour-pressure curve, whilst between 1,150°C. and 1,450°C. the curve becomes a straight line; in this region the pressure depends on the composition of the solid phase. Le Blanc and Eschmann (*Z. Elektrochem.* 1911, 17, 20) also found that the pressure above 1,200° depends on the nitrogen content of the solid phase as well as on the temperature, indicating that solid solutions are formed; they also found difficulty with the sublimation of calcium cyanamide.

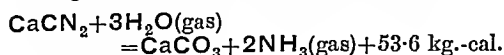
The action of fluxes, *e.g.*, calcium fluoride, on the reaction has been studied (Bredig, Fraenkel, and Wilke, *l.c.*; Foerster and Jacoby, *l.c.*; *ibid.* 1909, 15, 820; Gesellschaft für Stickstoffdünger, G.P. 163320, 1901). Calcium chloride lowers the temperature of absorption of nitrogen from 1,100° to about 800°, calcium fluoride to 900°. The fluxes probably remove a protecting film from the surface of the carbide. There is an optimum amount of fluoride, depending on the temperature.

The heat of formation of calcium cyanamide was determined, from the heat of combustion of a 98% specimen, free from carbon, as 84.0 kg.-cal. at constant volume and room temperature (Franck and Hockwald, *Z. Elektrochem.* 1925, 31, 581), which corresponds with a heat of reaction:

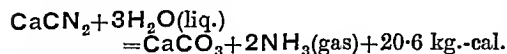


whilst the value 68.4 kg.-cal. was found from equilibrium measurements at 1,080–1,130° (Franck and Heimann, *ibid.* 1927, 33, 469). Kameyama (*J. Coll. Eng. Tokyo*, 1920, 10, 173) found 94.8 kg.-cal. (*cf. also* Matignon, *Ann. Chim. Phys.* 1908, [viii], 14, 1; Dolch, *Z. Elektrochem.* 1920, 26, 455; Ehrlich, *ibid.* 1922, 28, 529; Kameyama, *J. Fac. Sci. Tokyo*, 1923, 13, 61, 75; Kraso and Yee, *J. Amer. Chem. Soc.* 1924, 46, 1358; Franck *et al.*, *Samml. chem. u. chem.-techn. Vorträge*, N.F., 1931, 6; Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, 1931, 34, 325b; Gabrielson, *Trans. Sci. Inst. Ferti-*

lisers, Moscow, 1932, No. 92, 49; Barsky, Chim. et Ind. 1932, 28, 1032; Gelhaar, Tekn. Tidskr., Uppl. C. (Kemi), Stockholm, 1932, 62, 81; Aono, Bull. Soc. Chem. Japan, 1933, 7, 287). The heat of the hydrolysis reaction (Franck and Freitag, Z. Elektrochem. 1932, 38, 240) is:



or, with liquid water:



(Kameyama calculated 14.1 kg.-cal.; Landis estimated 200–300 C.H.U. per lb. of ammonia in autoclaves, J. Ind. Eng. Chem. 1916, 8, 156). The kinetics of cyanamide formation were studied by Franck, Hochwald, and Hoffmann (Z. physikal. Chem. Bodenstein Festb. 1931, 895).

The processes for the absorption of nitrogen by calcium carbide may be divided into: (i) those in which externally-fired retorts are used, and the process worked discontinuously; (ii) those in which the carbide is heated by electricity passed through a carbon rod in the mass of carbide, the process being worked discontinuously; (iii) those in which the carbide is passed continuously through an electric furnace in a current of nitrogen. At present, process (ii) is most used.

The overall power requirement for cyanamide production, including carbide, is 2.3 kw.-yr. (of 8,500 hour). per metric ton of nitrogen fixed; or, as 0.5 kw.-yr. is required per ton of carbide, and 4 tons of carbide are required to fix 1 ton of nitrogen as cyanamide, the power required for conversion of carbide to cyanamide alone is 0.3 kw.-yr. per metric ton of nitrogen fixed (Nitrogen Products Committee, Final Report, H.M. Stationery Office, 1919, p. 256).

Calcium cyanamide was first made in 1905 on a technical scale at Piano d'Orte, in Italy (Z. Elektrochem. 1906, 12, 551).

The process was then worked for a time in Norway. Cyanamide has been made at Niagara since 1909 (Landis, Lc.). Late in 1917 the American Cyanamid Co. formed a subsidiary company, the Air Nitrates Corporation, to erect the U.S. Nitrate Plant No. 2 at Muscle Shoals, Alabama, for a capacity of 110,000 tons of ammonium nitrate per annum, at a cost of £12,000,000 (Fairlie, Met. Chem. Eng. 1919, 20, 8; Jones, *ibid.* 1920, 22, 417). For various reasons, this factory never operated, but as it represents a large-scale plant of its kind a description of it is given below.

There are 16 rows of cyanamide furnaces, 96 in each row, or 1,536 in all. The cyanamide furnaces (Fig. 1) are 4 ft. 4 in. in outside diameter and 2 ft. 10 in. in inside diameter, and 5 ft. 4 in. deep. They are steel shells with 9-in. firebrick lining. To charge a furnace a cylindrical pasteboard or paper tube container 2 ft. 6 in. in diameter with a vertical paper tube 3 in. in diameter in the centre is inserted into the cold furnace and a charge of 1,600 lb. of milled carbide put in. There is an annular space of 2 in. between the paper and furnace wall. The carbon electrode is a  $\frac{5}{8}$ -in. pencil, 6 ft. 6 in. long,

inserted in the paper tube. The covers are put on and the outer cover luted with sand.

The nitrogen is brought in by an 8-in. pipe between each pair of furnaces and two  $1\frac{1}{2}$ -in. pipes carry off to the furnace, one to the bottom at the centre and the other at the side 6 in. above the bottom, each provided with a valve. The nitrogen reaches the furnace under 3–4 in. of water pressure.

Single-phase current of 100 v. and 200–250 amp. is turned on through the carbon rod for 20 minutes, and is then cut down to 50 v. and 100–115 amp. for 12 hours. The reaction gives out heat and is allowed to continue without current for 28 hours altogether. The temperature in the furnace is about 1,100°C.; the material does not melt, but sinters into a solid cake. The approximate composition of the product is  $\text{CaCN}_2$  63,  $\text{CaC}_2$  2,  $\text{CaO}$  13, and C 11%. It is pulverised so that 95% passes 200 mesh, all in an atmosphere of nitrogen. The milled material is fed at a controlled rate to the hydrating troughs, of which there are three, 36 ft. long and 3 ft. in diameter, each containing

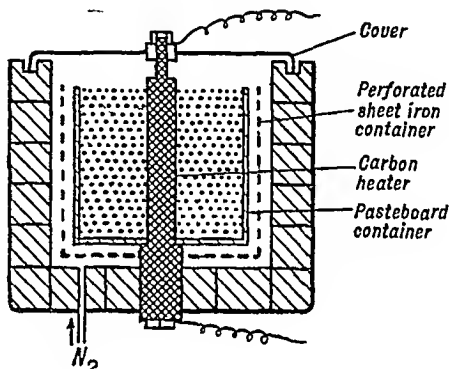


FIG. 1.

a horizontal shaft with projecting arms 20 in. long. Water is sprayed in at the feed end at a calculated rate to decompose the unchanged carbide. The material at the exit must be perfectly dry. The agitator rotates at 50 r.p.m. and conveys the material at the rate of 50 ft. per minute. The cyanamide is conveyed through an overhead tunnel to the ammonia autoclave building 300 ft. away.

The autoclaves (American Cyanamid Co., U.S.P. 1889956, 1932; Pascal, *Traité de Chimie minérale*, 1932, 3, 690; Landis, *Chem. Met. Eng.* 1916, 14, 87) are of steel and cylindrical, 8 ft. in diameter and 20 ft. high, each provided with a vertical agitator revolving 12 times per minute. A 2% solution of sodium hydroxide is run in to a depth of 9 ft. and 300 lb. of soda ash added, which reacts with the 13% of free lime in the cyanamide to form sodium hydroxide solution of about 3% strength (the addition of soda causes some loss of nitrogen as dicyanodiamide, etc.; Pascal, *Mém. Poudres*, 1924, 21, 1). The charge of 8,000 lb. of cyanamide is added from weigh bins. The acetylene from the 2% of still undecomposed carbide is allowed to escape through one valve through an exhaust fan. The outlet pipe is then

tightly closed and steam from special boilers admitted at 150 lb. for 20 minutes. Ammonia forms, the reaction being exothermic. When the pressure reaches 250 lb. the ammonia valve is opened cautiously, but the pressure is maintained for 3 hours. The pressure then falls and the ammonia is allowed to escape. The valve is shut again and steam admitted a second time for 20 minutes. The reaction proceeds at 200 lb. pressure for  $1\frac{1}{2}$  hours. The escaping gas contains 25% of ammonia and 75% of steam. It passes through a header and seven mud drums followed by seven ammonia column stills, each 10 ft. in diameter and 25 ft. high, containing 16 horizontal plates. The gas enters at the bottom and bubbles through caps over 4-in. holes in the plates, passing to 14 condensers arranged in seven sets of two in series, containing vertical tubes through which water circulates, where steam is condensed. The ammonia gas passes through a 28-in. pipe, tapped by two 20-in. mains, one conveying 55% of the ammonia to two 600,000 cu. ft. gasholders for the ammonia oxidation plant, and the other 45% to the neutralisation plant for ammonium nitrate. The capacity of the plant is 1,000 tons of ammonia gas per week.

The autoclave sludge is blown out through an 8-in. outlet at the bottom by means of steam or air and falls by gravity to 20 rotary filters, five spare, operating under 20-in. mercury suction, where the 2% sodium hydroxide solution is drawn off and returned to the autoclaves. Attempts have been made to use the corrosive sludge, e.g., in making cement (Baumann, *Chem.-Ztg.* 1920, 44, 562).

The cyanamide furnaces now used by North American Cyanamid, Ltd. at Niagara Falls are much larger than those at Muscelo Shoals, each taking 8,000 lb. of carbide and, with the use of larger carbide furnaces, the energy has been reduced from 22,000 kw.-hr. per metric ton of fixed nitrogen to 9,000 kw.-hr., including all accessory operations. The cyanamide may contain 23.5% of nitrogen. The capacity of the plant at Niagara Falls is 68,000 metric tons of fixed nitrogen per year (Lec, *Chem. Met. Eng.* 1931, 38, 564; M. de K. Thompson, "Theoretical and Applied Electrochemistry," New York, 1939, p. 479).

A different type of process is used in some of the German cyanamide works, but it is of little importance in comparison with the internal heating method.

It was found that calcium chlorido lowered the temperature at which nitrogen is absorbed by carbide to 700–800°, so that the reaction could be carried out in retorts externally heated by fuel. This process (G.P. 163320, 1901) was adopted by the A.G. für Stickstoffdünger at Westeregeln and at Knapsack, near Cologne. The latter works had a capacity of 11,000 tons of cyanamide per month. There are 10 carbide furnaces of the open rectangular type, charged by hand with a mixture of 100 parts of quicklime and 66 of anthracite. The main portion of the carbide is reduced to nut-size and is then mixed with 10% of calcium chlorido in tube mills, containing steel rods.

The mixture is fed to the cyanamide cans,

which are rectangular, 18 in. by 12 in. by 9 in., of thin sheet iron with a perforated bottom which can be removed in emptying. The bottom and sides are lined with paper before filling, and a piece of cardboard is laid on top of the charge. Fifteen cans are loaded on a car, which runs on a track the whole length of the furnaces.

There are 16 furnaces, about 120 ft. long and 6 ft. in diameter, of 2-in. iron plates, set in firebrick and heated by lignite gas. Nitrogen, from a Linde apparatus of 1,800 cu. m. per hour capacity, is fed in at the cooler end of the furnaces, and the carbide trucks run in at the opposite end. Every 8 hours three cars are pushed into the furnace by an electric ram. At the end of 24 hours, three cars, or 45 cans, of cyanamide have reached the nitrogen end of the furnace, are pushed out, and allowed to cool. The product is then ground in the same manner as the carbide. It contains 16–22% of nitrogen and 0.75% of calcium carbide (Allmand and Williams, *J.S.C.I.* 1919, 38, 301n). A similar process is in use in the Rumanian factory at Söras (Matignon, *Chim. et Ind.* 1922, 7, 26; *J.S.C.I.* 1922, 41, 178r).

A continuous method was described by Tofani (G.P. 246077, 1910). The method of Carlson (*Chem.-Ztg.* 1917, 41, 562) is used by the Ljunga Verk, Stockholms Superfosfat Fabriks Aktiebolag, Stockholm, which produced 20,000 tons of cyanamide annually (B.P. 123796, 1918; A. B. Nitrogenium, G.P. 325152 and 330165, 1916). In this, shaft-furnaces with shelves are used, and the mixture of carbide, with an indifferent substance such as lime, and 3.5% of calcium chloride or fluoride, drops across heating electrodes and is moved from shelf to shelf down the furnace. There are 8–10 shelves per furnace, with automatic rakes for moving the carbide. The absorption of nitrogen is 80%. In the Tofani furnace the powder was dropped directly down the furnace, and the contact with the gas was much less complete. The product obtained in the Carlson furnace is in the form of coke-like lumps a few inches in diameter, instead of a hard solid cake. It is taken out by opening a hole at the bottom, constructed as a double lock. The heating is effected by an electric arc in each furnace, the consumption of electrodes being 3–5 kg. per metric ton of cyanamide. The output of each furnace is 20–25 tons of cyanamide per 24 hours. About 15 kw.-hr., measured at the furnace, are used per kg. of nitrogen fixed in the form of cyanamide, as compared with 20 kw.-hr. in discontinuous processes, and the product contains about 20% of combined nitrogen. The advantages claimed for the process are: reduction in carbide consumption to 720–730 kg. of carbide of 300 l. per ton cyanamide; a saving of 10% on erection costs; a product richer in combined nitrogen; and lower working costs consequent on the use of a continuous process. The process, however, is used only in a limited number of works.

The German cyanamide factories (with capacities in metric tons of nitrogen per year) were at Trostberg (50,000), Piesteritz (40,000), and Waldshut (14,000), using the Frank-Caro

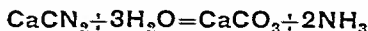
process, and Knapsack (20,000), using the Polzenius process (Chem. Trade J. 1933, 93, 290). The process has been improved, the furnaces being enlarged, and purer raw materials used, so that the nitrogen content of the product has been raised to 20.6%, and the power consumption reduced from 18–20 kw.-hr. to 10 kw.-hr. per kg. of nitrogen (*ibid.* 1931, 88, 102; J.S.C.I. 1929, 48, 74x; Enke, *Tonind.-Ztg.* 1932, 56, 1137). The production increased from 44,000 tons of nitrogen in 1924 to 95,000 tons of nitrogen in 1929, and new works have since been put into operation (Chem. Trade J. 1931, 88, 102; cf. Gall, *Chim. et Ind.* 1921, 6, 430; Kahn, *Metallbörse*, 1928, 18, 1295, 1406, 1463; Krauss, Pohlmann, and Wagner, in Ullmann, "Enzyklopädie der technischen Chemie," 2nd ed., Vol. VIII, p. 1; Franck, Makkus, and Janke, "Der Kalkstickstoff," in *Samml. chem. n. chem.-techn. Vorträge*, N.F., 1931, 6).

There are large cyanamide factories in France (Bellegarde; Lannemezan), Russia, Yngoslavia, and Japan. The process is one of the major nitrogen fixation methods: in 1938 (the last year for which complete statistics are available) the production of ammonium salts by the two main synthetic processes, expressed in thousands of metric tons of nitrogen, was: synthetic ammonia 533, cyanamide 321 (*see* p. 552d).

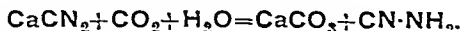
**Uses of Cyanamide**—Besides its use as a source of ammonia, crude cyanamide (the  $\text{CaCN}_2 + \text{C}$  mixture) finds other uses. After suitable treatment by hydration, oiling, granulation, etc., to render it less corrosive and dusty (*see* B. Waesser and E. Fyelman, "The Nitrogen Industry," Churchill, 1926, Vol. II, pp. 373, 412; American Cyanamid Co., F.P. 738685, 1932; for poisoning by cyanamide, *see* Linneberg, *Amer. Chem. Abstr.* 1933, 5419) it is used directly as a fertiliser. It deteriorates on storage (Jacob, Krase, and Braham, *Ind. Eng. Chem.* 1924, 16, 684) and is best kept in a dry place in sacks covered with dry sand (Zeleski, *Przemysl Chem.* 1931, 15, 271). In the preliminary treatment, the free lime is hydrated with water and the dry hydrated material treated with mineral oil or tar oil; in this treatment there is an increase in weight of about 10% of the cyanamide, but the nitrogen content is reduced, usually to about 16% (E. C. Worden, "Technology of Cellulose Esters," Spon, 1921, Vol. I, ii, p. 929). In the Gros process the hydration is carried out in two stages (7% and 10%) with the cyanamide in a thin layer on an endless conveyor, the moist mass being then passed between two cylinders, one perforated with  $\frac{1}{8}$ -in. holes through which it is pressed out in small rods about  $\frac{3}{8}$  in. long. There is a loss of about 3% of fixed nitrogen as ammonia. The raw untreated material is sometimes called "nitrolim" and the treated product "cyanamide."

In British conditions the fertilising value of cyanamide nitrogen is about 94% that of ammonia nitrogen, but the function of the lime formed on hydrolysis in fixing nitric acid formed by nitrification of the ammonia is an important factor. In Egypt, cyanamide does not undergo sufficiently rapid nitrification to satisfy the

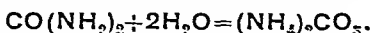
needs of quickly growing crops, for which calcium or ammonium nitrate is preferable (Russell, J.S.C.I. 1917, 36, 256; Hendrick, *ibid.* 1918, 37, 146x; E. J. Pranke, "Cyanamid," Easton, Pa., 1913). The mode of decomposition of cyanamide in the soil is not simple (*see* Cowie, J. Agric. Sci. 1919, 9, 113; Mazé, Vila, and Lemoigne, *Compt. rend.* 1919, 169, 804, 921; Sir A. D. Hall, "Fertilisers and Manures," Murray, 1929; Lefort des Ylouses, *Chim. et Ind.* 1927, 18, 216). On exposure to moist air, small quantities of ammonia are liberated:



but free cyanamide is also formed:

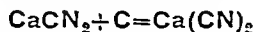


The latter may then combine with water to form urea:  $\text{CN}\cdot\text{NH}_2 + \text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$ . Urea is converted by fermentation into ammonium carbonate:



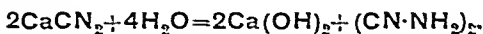
The latter is readily oxidised to nitrates in the soil. Other substances may be formed, such as basic calcium cyanamide, and dicyanodiamide ( $\text{CN}\cdot\text{NH}_2$ )<sub>2</sub>; the latter compound has been said to be prejudicial to crop growth (*see* Pranke, *l.c.*), but this has not been confirmed.

Besides its use as a fertiliser, cyanamide is also a source of various chemicals. It is converted to cyanide by fusion with a flux:



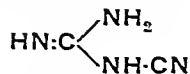
(*v.* CYANIDES, Vol. III, 488b), and from cyanide, hydrocyanic acid for fumigation is prepared.

Dicyanodiamide ( $\text{CN}\cdot\text{NH}_2$ )<sub>2</sub> (Anon., *Z. angew. Chem.* 1903, 16, 520; *v.* Vol. III, 602d), formed by the action of cold water on calcium cyanamide:

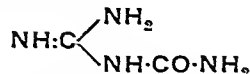


is used in the manufacture of dyes, and in reducing the temperature of explosion when mixed with explosives such as cordite, which alone rapidly destroy the rifling of guns.

When calcium cyanamide is treated with acids or alkalis, cyanoguanidine,



and dicyanodiamidine,



are formed, from which urea and guanidine may be obtained (Morrell and Burgen, J.C.S. 1914, 105, 576; Grube and Kruger, *Z. physikal. Chem.* 1913, 86, 65; Grube and Motz, *ibid.* 1925, 118, 145). Guanidine is prepared by heating with acids in an autoclave. Guanidine nitrate and nitroguanidine are used as deterrents in explosives. Urea may be obtained directly from calcium cyanamide by treating with 10–20% sulphuric acid at 20–25°, and is proposed as an effective fertiliser:





Veronal and creatin are also produced from cyanamide, and lead and copper cyanamides are said to be of technical importance (Carlson, *Z. angew. Chem.* 1914, 27, iii, 724; E. J. Pranke, "Cyanamid," Easton, Pa., 1913). "Ferrodur" is a material containing calcium cyanamido used in case hardening.

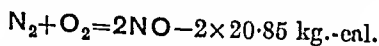
Many methods for the analysis of cyanamido have been proposed (Perotti, *Gazzetta*, 1905, 35, ii, 228; Caro, *Z. angew. Chem.* 1910, 23, 2405; Brioux, *Ann. Chim. Analyt.* 1910, 15, 341; Stutzer and Söll, *Z. angew. Chem.* 1910, 23, 1873; Kappen, *Chem.-Ztg.* 1911, 35, 950; Monnier, *ibid.*, p. 601; Stutzer, *ibid.*, p. 694; Kirchhoff, *ibid.* 1912, 36, 1058; Grubo and Krüger, *Z. angew. Chem.* 1914, 27, 326; Morell and Burgen, *J.C.S.* 1914, 195, 576; Weston and Ellis, *Seventh Internat. Congress Appl. Chem.* London, 1909, Rep. Sect. I, p. 69; Kameyama, *J. Coll. Eng. Tokyo*, 1920, 10, 173). The best method is to determine the nitrogen content by the Kjeldahl method (E. Berl and G. Lunge, "Chem.-tech. Untersuchungsmethoden," Berlin, 1932, Vol. II, i, p. 572; see also *Ergänzungswerk*, ed. by J. D'Ans, Vols. II and III, 1939-40). Some analyses of different specimens of cyanamide (P. Pascal, "Traité de Chimie minérale," Masson, 1932, Vol. III, p. 683) are:

CaCN <sub>2</sub> .	N.	CaC <sub>2</sub> .	Ca <sub>3</sub> P <sub>2</sub> .
59.90	21.00	0.3	0.25
51.48	18.00	0.105	0.024
46.90	16.40	0.150	0.023
C.	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	CaO.	SiO <sub>2</sub> .
12.0	5.1	19.0	2.3
11.82	6.72	25.21	4.30
11.96	8.12	27.82	4.30

#### THE ARC PROCESS.

Cavendish in 1784 (*Phil. Trans.* 1784, 74, 119; 1783, 78, 261; J. R. Partington, "The Composition of Water," Bell, 1928, p. 17) observed the formation of nitric acid when oxygen containing nitrogen is exploded with hydrogen (in the explosion of air with hydrogen, no nitric acid is formed, as the flame temperature is too low), and of potassium nitrate when condensed sparks are passed through a mixture of air and oxygen confined over potash solution. Lord Rayleigh (*J.C.S.* 1897, 71, 181) used a glass globe of 50 l. capacity, containing a mixture of 9 vol. of air and 11 vol. of oxygen, in which an electric arc was burning. The resulting oxides of nitrogen were absorbed by allowing a fountain of sodium hydroxide solution to play over the inside of the globe. This also served to keep the vessel cool. An absorption of 21 l. of gas per hour was obtained with 0.8 kw., which gives a production of 46 g. of nitric acid per kw.-hr. In the most efficient modern arc furnaces the yield is 62 g. HNO<sub>3</sub> per kw.-hr.

Crookes in 1892 (*Chem. News*, 1892, 65, 301) had shown that atmospheric nitrogen and oxygen burn with a true flame when a high-tension electric discharge passes through air, nitric oxide being formed by an endothermic reaction:



McDougall and Howles (*Mem. Manchester Phil. Soc.* 1900, [iv], 44, No. 13) in Manchester, and

Bradley and Lovejoy at Niagara (U.S.P. 709868, 1902; M. de K. Thompson, "Theoretical and Applied Electrochemistry," New York, 1925, p. 498), unsuccessfully attempted to utilise the arc process technically, since, although the yields were favourable, the apparatus was very complicated and subject to breakdown.

The first successful industrial application of the arc process was made by K. Birkeland and S. Eyde (*Trans. Faraday Soc.* 1906, 2, 98; U.S.P. 837277, 1906) in 1905 at Notodden, in Norway, where conditions for obtaining cheap electric energy from water power are very favourable. The power at Notodden is derived from the Svaegfoss, about 1½ miles up the valley, and the water passing over the Rjukanfoss generates in its passage to the Hitterdal lake 40,000 h.p. at the Svaegfoss, 16,000 h.p. at the Lienfoss, and 20,000 h.p. at the Tinfoss, making a total of 75,000 h.p. available at Notodden. A new works was later established at Rjukan, at a cost of £3,000,000, with 300,000 h.p. available. The power for this is derived from the Rjukan fall, the water of which is collected in the Moesvand Lake, with a capacity of 768,000,000 cu. m. This reservoir is closed by a large dam and feeds the river Maana, the water of which is conducted through a tunnel, 4 km. long and 26 sq. m. in section, to a collecting house, from which it passes through ten steel conduits or flumes, 2 m. in diameter, carrying 50 cu. m. of water per second to the Rjukanfoss power house, which is 110 m. long and 20 m. wide, and houses ten turbines, each of 14,500 h.p., directly coupled to the generators. The current is transmitted through sixty cables, some of copper and some of aluminium, to the Rjukan I works at Vernork and the Rjukan II works at Saaneim, both approximately the same size (J. R. Partington and L. H. Parker, "The Nitrogen Industry," Constable, 1922, p. 245).

Another factory, formerly owned by the Norwegian company, is situated at Pierrefitte, on the French side of the Pyrenees, where water power from two lakes is used. This works used 8,000 kw., producing 4,000 tons of nitric acid per annum. The water is obtained from the lake at Canterets, at an altitude of 280 m., and that at Luz St. Sauveur, at an altitude of 140 m. It is conducted through six flumes, running down the Pic de Soulon, three to each lake, and 3 ft. and 4 ft. in diameter, respectively. The high-pressure water passes to Pelton wheels and the low-pressure to turbines, in each case directly coupled to alternators. These also supply power for the electrified portion of the Midi Railway from Lourdes to Canterets. The current is transformed to 10,000 v. for transmission to the works (Partington and Parker, *op. cit.*). This works now makes synthetic ammonia by the Casale process.

The arc process at Rjukan has since 1928 been replaced by a synthetic ammonia and ammonia oxidation plant with a capacity of 140,000 tons of combined nitrogen per annum, with the same power expenditure as for 35,000 tons by the arc process. The hydrogen is made electrolytically at Vernork and sent by pipe-line to Rjukan. The nitrogen is obtained by burning hydrogen in air. The I.G. Farbenindustrie A.-G. had



an interest in the process (J.S.C.I. 1931, 50, 320; Chem. Trade J. 1933, 93, 266; Coutourier, Chim. et Ind. 1933, 29, 463). The arc process with 25 furnaces of 4,000 kw. was still operating at Notodden in 1939 (M. de K. Thompson, "Theoretical and Applied Electro-chemistry," New York, 1939, p. 475).

The arc process used a large amount of energy, 8.35-8.4 kw.-yr. per ton of nitrogen fixed.

For the equilibrium constant of the reaction  $N_2+O_2\rightleftharpoons 2NO$  Nernst (Gött. Nachr. 1904, 261; Z. anorg. Chem. 1906, 45, 126; 1906, 49, 213; Finckh, *ibid.* 1905, 45, 116; Jellinek, *ibid.* 1906, 49, 229) gives an expression which may be simplified to

$$\log \sqrt{K}=0.5441-4725.5/T$$

where  $T$  is the absolute temperature and

$$K=C_{NO}^2/C_{N_2}\times C_{O_2}.$$

In the case of air, when  $x\%$  of nitric oxide by volume has been formed in equilibrium,  $K=x^2/(79.2-\frac{1}{2}x)(20.8-\frac{1}{2}x)$ , and, therefore, since  $x$  is small,  $x=40.8\sqrt{K/(1+0.62\sqrt{K})}$ . From these equations the values of  $x$ =percentage of nitric oxide in Table I have been calculated. They agree fairly well with the observed values, which were obtained by exploding a mixture of electrolytic gas and air, and by drawing air through platinum and iridium tubes heated electrically.

TABLE I.—EQUILIBRIUM YIELDS OF NO IN AIR.

Temperature, °K.	% NO by volume (obs.).	% NO by volume (calc.).
1,811	0.37	0.35
1,877	0.42	0.43
2,033	0.64	0.67
2,195	0.97	0.98
2,580	2.05	2.02
2,675	2.23	2.35
3,200	5.0 about	4.39

The same values of  $K$  apply, of course, to any initial mixture of nitrogen and oxygen as well as air, but the relation between  $x$  and  $K$  is different for each mixture. For the important case of equal volumes of oxygen and nitrogen  $K=x^2/(50-\frac{1}{2}x)(50-\frac{1}{2}x)$ , or, since  $x$  is small,  $x=50\sqrt{K/(1+0.5\sqrt{K})}$ . The increased yield with the mixture  $N_2+O_2$  as compared with air is, therefore, approximately 18%. Oxygen has a thermal conductivity 7% greater than that of nitrogen. Haber and Koenig (Z. Elektrochem. 1907, 13, 725) obtained 14.5% of nitric oxide from  $N_2+O_2$ . By using a short arc in a water-cooled tube these experimenters (*ibid.* 1908, 14, 689) obtained 17.8% of nitric oxide. The same final concentration was obtained with  $N_2+O_2$  and NO as initial gas, indicating equilibrium. Increase of pressure does not increase the yield. Similar experiments were made by Holwech (*ibid.* 1910, 16, 369), Haber and Holwech (*ibid.* p. 810), Holwech and Koenig (*ibid.*, p. 803—cooled arcs), Haber, Koenig, and Platou (*ibid.*, pp. 789, 796). The yields for a given expenditure of energy are much larger than those of Nernst; in the most favourable cases they amount to

80 g. of nitric acid per kw.-hr. The percentage of nitric oxide in the resulting gases also corresponds, on the thermodynamic theory, with impossibly high temperatures (the temperature 3,200° corresponds with only about 5% of nitric oxide, as is seen from Table I). Haber considered that a cool arc is more favourable to nitric oxide formation than exposure to very high temperatures followed by rapid cooling, and that electronic impacts play a part under certain conditions.

Experimental investigations of the formation of nitric oxide in arc discharges indicate that an electrical effect, probably connected with the electron emissive power of the material of the electrodes, plays a part, as well as the main thermal effect, and that the equilibrium percentages  $x$  of nitric oxide are greater than those found by Nernst, Jellinek, and Fink (NJF); the following results include also those of Briner, Boner, and Rothen (BBR) (Schwab and Loeb, Z. physikal. Chem. 1925, 114, 23; McCollum and Daniels, Ind. Eng. Chem. 1923, 15, 1173; Briner, Boner, and Rothen, J. Chim. phys. 1926, 23, 788; Helv. Chim. Acta, 1926, 9, 634; Karrer, Trans. Amer. Electrochem. Soc. 1925, 48, 223; H. Pauling, "Elektrische Luftverbrennung," Halle, 1929; calculated values in Giaque and Clayton, J. Amer. Chem. Soc. 1933, 55, 4875):

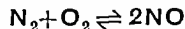
$T^\circ K.$	1,181	1,877	2,033	2,195	2,580
$x$ NJF.	0.37	0.42	0.64	0.97	2.05
$x$ BBR.	0.65	0.79	1.25	1.86	3.89
$x$ Nernst's theorem	0.63	0.78	1.20	1.82	3.81

The results are expressed by

$$\log C_{NO}=-4,726/T+\frac{1}{2}\log (C_{N_2}\cdot C_{O_2})+0.81$$

(Shilling, Trans. Faraday Soc. 1926, 22, 377). Reduced pressure (Colin and Tartar, J. Physical Chem. 1927, 31, 1539) and presence of moisture (Tartar and Perkins, *ibid.* 1926, 30, 595) lower the yield of nitric oxide. At 100 cm. pressure, Briner (Bull. Soc. chim. Belg. 1928, 37, 169) obtained an optimum concentration of 12-14.5% of nitric oxide. Better yields are obtained by increasing the oxygen concentration (Colin and Tartar, *l.c.*); coating the electrodes with barium and other oxides increases the efficiency parallel with the thermionic emissivity (Briner and Rivier, Helv. Chim. Acta, 1929, 12, 881; Briner and Wakker, F.P. 745840, 1932).

The velocities of formation and decomposition of nitric oxide have been determined. Below 3,000° the reaction is bimolecular:



above 3,000° it is said to be unimolecular (Le Blanc and Nüranen, Z. Elektrochem. 1907, 13, 297). In the bimolecular case, the velocity equation is:

$$dx/dt=k_1(C_0-\frac{1}{2}x)(C_N-\frac{1}{2}x)-k_2x^2$$

where  $C_N$  and  $C_O$  are the initial concentrations of nitrogen and oxygen in percentages by volume, and  $x$  the percentage of nitric oxide present at a given instant. The velocity constants  $k_1$  and  $k_2$ , representing the rate of formation and decomposition of nitric oxide,

respectively, for unit concentrations, have been determined experimentally by Jellinek (Z. Elektrochem. 1907, 13, 297; Z. anorg. Chem. 1906, 49, 229), whose results are given in Table II. The time for half decomposition of pure nitric oxide into nitrogen and oxygen is very approximately  $t_2=1/k_2$ ; the time for half the possible nitrification of air, i.e., half the theoretically possible production of nitric oxide, is approximately  $t_1=1.36/\sqrt{k_1k_2}$ . The velocity constants depend very much on the temperature; Steinmetz (Chem. Met. Eng. 1920, 22, 299) calculates from Jellinek's results

$$\log k_2 = 11.113 + 5.731 \times 10^{-3}T,$$

when  $t$  is in seconds. From this, and the relation  $k_1=k_2K$ , the values given in Tables II and III have been calculated. The values of  $K$  have been obtained from the formula:

$$\log K = 1.048 - 9,380/T$$

given by Steinmetz, which is in good agreement with the formula of Nernst previously quoted.

TABLE II.—VELOCITIES OF DECOMPOSITION OF NITRIC OXIDE.

Time in minutes for 50% decomposition of pure nitric oxide at atm. press. into nitrogen and oxygen.

Temperature, °K.	Time in min., obs.	60 <i>t</i> <sub>2</sub> min., calc. = 1/ <i>k</i> <sub>2</sub>	<i>k</i> <sub>2</sub> for second as unit of time.
900	7.35 × 10 <sup>3</sup>	8.9 × 10 <sup>3</sup>	1.87 × 10 <sup>-6</sup>
1,100	5.80 × 10 <sup>2</sup>	6.4 × 10 <sup>2</sup>	2.01 × 10 <sup>-5</sup>
1,300	4.43 × 10	4.5 × 10	3.66 × 10 <sup>-4</sup>
1,500	3.30	2.35	5.12 × 10 <sup>-3</sup>
1,700	2.47 × 10 <sup>-1</sup>	2.33 × 10 <sup>-1</sup>	7.17 × 10 <sup>-2</sup>
1,900	1.74 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	1.002
2,100	1.21 × 10 <sup>-3</sup>	1.18 × 10 <sup>-3</sup>	1.41 × 10
2,300	8.40 × 10 <sup>-5</sup>	8.45 × 10 <sup>-5</sup>	1.07 × 10 <sup>2</sup>
2,500	5.76 × 10 <sup>-6</sup>	6.06 × 10 <sup>-6</sup>	2.75 × 10 <sup>3</sup>
2,700	3.92 × 10 <sup>-7</sup>	4.43 × 10 <sup>-7</sup>	3.85 × 10 <sup>4</sup>
2,900	3.35 × 10 <sup>-8</sup>	3.08 × 10 <sup>-8</sup>	5.40 × 10 <sup>5</sup>
3,100	2.25 × 10 <sup>-9</sup>	2.20 × 10 <sup>-9</sup>	7.57 × 10 <sup>6</sup>
3,500	—	1.13 × 10 <sup>-11</sup>	1.48 × 10 <sup>9</sup>
4,100	—	4.10 × 10 <sup>-15</sup>	4.07 × 10 <sup>12</sup>

TABLE III.—VELOCITY OF FORMATION OF NITRIC OXIDE FROM AIR.

Time in minutes for production of half the theoretically possible amount of nitric oxide.

Temperature, °K.	Time in min., obs.	60 <i>t</i> <sub>1</sub> min., calc. = 1.30/√ <i>k</i> <sub>1</sub> <i>k</i> <sub>2</sub>	<i>k</i> <sub>2</sub> for second as unit of time.
900	—	—	7.89 × 10 <sup>-16</sup>
1,500	1.81 × 10 <sup>3</sup>	1.77 × 10 <sup>3</sup>	3.19 × 10 <sup>-8</sup>
1,700	5.90 × 10	5.45 × 10	2.43 × 10 <sup>-6</sup>
1,900	2.08	1.99	1.29 × 10 <sup>-4</sup>
2,100	8.43 × 10 <sup>-2</sup>	8.22 × 10 <sup>-2</sup>	5.36 × 10 <sup>-3</sup>
2,300	3.75 × 10 <sup>-3</sup>	3.76 × 10 <sup>-3</sup>	1.84 × 10 <sup>-1</sup>
2,500	1.77 × 10 <sup>-4</sup>	1.85 × 10 <sup>-4</sup>	5.44
2,700	8.75 × 10 <sup>-6</sup>	9.60 × 10 <sup>-6</sup>	1.44 × 10 <sup>2</sup>
2,900	5.75 × 10 <sup>-7</sup>	5.20 × 10 <sup>-7</sup>	3.52 × 10 <sup>3</sup>
3,100	3.10 × 10 <sup>-8</sup>	2.87 × 10 <sup>-8</sup>	7.90 × 10 <sup>4</sup>
3,500	—	10 <sup>-10</sup>	3.46 × 10 <sup>7</sup>
4,100	—	2.3 × 10 <sup>-14</sup>	2.34 × 10 <sup>11</sup>

From these results it follows that the best results should be obtained when the air is heated to a temperature not less than 3,000°, and then cooled with all possible speed below the temperature, say 1,000°, at which the velocity of decomposition of the nitric oxide formed at the higher

temperature has become inappreciable. This conclusion is confirmed by experiment. Since the rapidity of cooling attainable practically limits the amount of nitric oxide remaining, there will be no point in going above a certain temperature in the arc.

In the commercial operation of the arc process, a concentration of 2% of nitric oxide by volume is attained as a maximum from air, and usually only a little over 1%. The temperature corresponding to 2% is about 2,500°. It is thus possible to calculate the minimum expenditure of energy necessary. This is the electrical equivalent of the heat absorbed in the reaction  $N_2 + O_2 = 2NO$ , plus that required to raise the temperature of the gases to 2,500°. Since the mean specific heats of the three gases at constant pressure are approximately equal, and given by 6.8+0.0006*t* g.-cal. per g.-mol., we have, as the absorption of energy for heating 14 g. of nitrogen and 16 g. of oxygen to 2,500°:

$$\frac{1}{2}(6.8 + 2,500 \times 0.0006) = 20,600 \text{ g.-cal.}$$

If we add to this the energy 21,600 g.-cal. (cf. p. 519*d*) for the production of 30 g. of nitric oxide (100% conversion), we find as the minimum energy required 20,600+21,600=42,200 g.-cal., or about 0.05 kw.-hr. But in practice it is found necessary to expend 1 kw.-hr. (2% conversion) in the formation of 30 g., or 1 g.-mol., of nitric oxide, hence the energy efficiency of the arc process is  $0.05 \times 100 = 5\%$ . A certain amount of this energy is recoverable in the less available form of heat from the hot gases, by passing the latter through boiler tubes. The maximum amount so recoverable is about 5% of the initial energy after all requirements for evaporation and cooling have been met, the latter utilising about 8%. The arc process as operated is clearly very wasteful of energy, only about 10% being usefully applied. It can, therefore, be used economically only when a very cheap source of energy is available. This is provided by large water-power sources, or, in Germany, by the utilisation of brown coal (or lignite) from which electrical energy is produced at a cost of about 0.4*d*. (2.8 pfg.) per kw.-hr. In Great Britain such cheap power could be obtained only by some such source as the proposed Severn Barrage (Nature, 1933, 131, 449).

#### The Birkeland and Eyde Process.—

In this type of furnace the arc is maintained by an alternating current and is spread by a strong magnetic field at right angles to the axis of the electrodes. The current filament tends to move at right angles to its length in the magnetic field, and is blown into a semicircle at each half period of the current. The filament breaks when the resistance along it is greater than that of a new arc in the cooler air between the points of the electrodes (Trans. Faraday Soc. 1906, 2, 98; J. Roy. Soc. Arts, 1909, 57, 568). The semicircles succeed each other with great rapidity on each side of the electrode axis, and the impression on the eye is that of a steady circular sheet of flame (Andriessens, Z. Elektrochem. 1919, 25, 255).

The electric flame is produced in a flat box of refractory material (Fig. 2), the walls of which do not in actual working become heated beyond

1,000°C. The electrodes are U-shaped copper tubes, 1 in. wide, separated at the ends by a  $\frac{1}{8}$  in. gap for the arc. The position of the electrodes is regulated by screws outside the furnace. One electrode is earthed. The applied voltage is 6,500. In a recent type the air is aspirated into the furnace through grids of iron netting opposite the inlet ports; in the older types the air was forced through by Root's blowers. The air is divided by channels in the fireclay lining, so as to be directed uniformly on both sides of the arc flame. During the brief contact of the air with the intensely hot flame some combination of oxygen and nitrogen takes place. The gases are then swept out of the furnace and cooled with great rapidity to about 1,000°, below which temperature nitric oxide is stable.

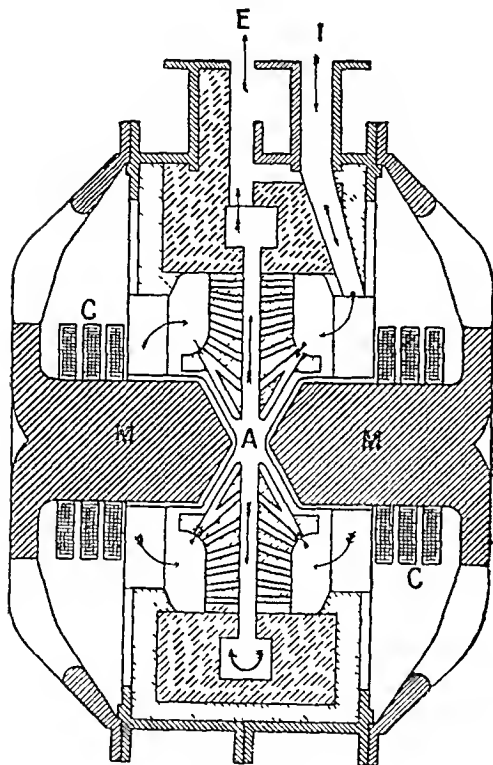


FIG. 2.

The electrodes are cooled by a rapid current of water passing through them. The latest types of Birkeland and Eyde furnaces were made in units taking 2,000, 3,000, or 4,000 kw. The most economical size is said to be 3,000 kw. The electrodes last 3-4 weeks, and are easily replaced in about 15 minutes when required. The temperature of the flame is estimated at 3,000-3,500°; that of the escaping gases, of which about 74 cu. ft. pass through the furnace per kw.-hr., is about 1,000°.

The concentration of nitric oxide in the gas leaving the furnace is about 1.25% by volume. The oxides of nitrogen are absorbed as nitric acid and as sodium nitrate and nitrite. About 97% of the fixed nitrogen is absorbed, 85% of this as 30% nitric acid and 15% as nitrite. The energy consumption in the Birkeland-Eyde

process is estimated as 1 kw.-hr. per 61 g. of nitric acid  $\text{HNO}_3$  for overall working.

The gas in the main leading from the furnace enters at a temperature of about 900° into the fire-boxes of Babcock boilers, in which steam in excess of all requirements in the works is raised. After passing through the boiler fire-box the gas leaves at about 250° to pass through the coolers. These are placed in the open air, and consist of four batteries of iron tubes, cooled in vertical tanks through which water flows.

The gas leaves the coolers for the oxidation tower, of sheet iron and of sufficient capacity to give one minute contact to the gas to enable the nitric oxide to be partly converted into nitrogen peroxide before contact with water. The gas leaves at 50° and enters the absorption towers, constructed of slabs of Norwegian granite clamped by iron bands. The towers are 10-sided, 26.925 m. high inside and of 7.3 m. uniform external diameter. The thickness varies from 350 mm. at the bottom, in steps of 300, 250, and 200 mm. to the top. They are mounted on concrete piers with all joints visible and accessible in case of leakage. The towers are completely packed with pieces of Norwegian quartz about the size of walnuts. The gas enters at the bottom of the first tower and alternately at the top and bottom of successive towers. Acid is circulated in each tower by one montejus of iron-clad acid-resisting stoneware, having a capacity of 400 l. The delivery is intermittent, the montejus emptying once every two or three minutes. There is one 4-in. stoneware pipe to each tower, with rubber joints, for circulation in that tower, and a similar pipe for transferring acid from the next tower of the series. The circulation amounts to 10,000 l. of acid per hour. The top of the tower is domed, in sections joined with blue asbestos covered with tar.

The acid flows from each tower into a large granite tank with an aluminium cover, from which it is taken to the montejus. The acid from the first tower, which is the strongest, is about 30% nitric acid. This can be raised to 52% by slower circulation, but the weaker acid gives the best all-round efficiency of absorption. The strengths in the succeeding towers are usually 20, 10, and 5%, respectively. The time of passage of the gas through each tower is of the order of 1 minute.

After leaving the fourth acid tower, the gas enters an alkali absorption tower of sheet iron, about the same size as the acid towers, and also packed with quartz. Through this tower a solution of sodium carbonate, containing about 2% of sodium hydroxide, is circulated. Sodium nitrate and nitrite are formed.

The time of passage of the gas through the alkali tower is 1 minute; it is then practically (but not quite) free from oxides of nitrogen, and passes through fans to the open air.

The acid may be concentrated or converted into calcium nitrate. The sodium nitrate and nitrite are evaporated and sold for use in sulphuric acid chamber plants, or the nitrite is recovered in crystals for dye-making and other purposes.

**Concentration of the Nitric Acid.**—The nitric acid is concentrated in a very efficient

apparatus, due to Collett (F.P. 357221, 1905; 450448, 1912; U.S.P. 854928, 1907, and 1079541, 1913).

The 30% acid is pumped to a reservoir from which it descends to four granite towers, 10 ft. in diameter and 50 ft. high, lined with acid-resisting stone and packed with quartz. In these it meets with steam from the weak acid concentrating plant, next described, and receives a preliminary concentration. The acid before entering the towers is also preheated by waste steam from another part of the plant. The concentration apparatus proper consists of steam-jacketed tubes. To each preliminary tower is attached a battery of four sets of four silicon iron tubes, i.e., 16 tubes in all. Four tubes are arranged vertically around a bell-shaped head, and steam at 115 lb. is passed through the jackets. Four of these evaporators form a unit attached to each of the four towers. Evaporation is effected at atmospheric pressure and the acid brought to 60%  $\text{HNO}_3$ . The 60% acid is collected in four granite reservoirs, and is pumped from these to a single large reservoir at the top of the building, from which it flows to two octagonal granite towers, 8 ft. in diameter and 30 ft. high, one being in reserve. Into the same tower flows a stream of 80% sulphuric acid from a tank alongside the 60% nitric acid tank. Nitric acid of 96-97% strength is distilled over and is condensed in aluminium S-pipes placed between the two towers. The acid collected is sent down a small granite tower through which compressed air is passed to remove oxides of nitrogen, which pass to the absorption plant. The diluted sulphuric acid (60-65%) is concentrated in an apparatus similar to that used for making the 60% nitric acid, except that it works under vacuum, maintained by a vertical fall-pipe and water condensing jet. The strong acid is transported in strong earthenware bottles, holding 80 gallons.

*Sodium Nitrate* is prepared from the liquor obtained from the alkali tower, or by neutralising the tower acid with soda-ash, the oxides of nitrogen evolved being removed by fms. Sodium nitrite is concentrated in an apparatus similar to that used for nitric acid, the final concentration being carried out in five pans, 5 ft. by 20 ft. by 2 ft., heated by steam coils. Both salts are dried in hydro-extractors and Bühler's drying apparatus (Fig. 3), and bagged.

The Bühler drier has an air heater A and a fan B for forcing air at 100° through the apparatus. The salt enters on a roller C and is carried by the air current into the cyclone D. The dry powder is taken out into casks through the rollers K and the air is filtered in E and escapes through H. The time of passage of the salt through the apparatus is 5-7 seconds.

*Calcium Nitrate*.—The nitric acid from the towers is run through a series of granite tanks filled with limestone, until the liquid contains not more than 0.5% of nitric acid, which is neutralised by the addition of lime. The liquid is then evaporated in vacuum pans until it has  $\rho$  1.9, and run into iron drums holding 380 l., when it sets to a hard mass and is thus exported for chemical purposes; or it is run on to shallow trays and when cold is broken up, ground to a

coarse powder, and sent out as manure in wooden casks. It varies in appearance from red-brown to black, according to the nature of the limestone from which it is made, and has the following composition:

N=13.1%, corresponding to 77.0%  $\text{Ca}(\text{NO}_3)_2$   
 Water . . . . . 21.5%  
 Insoluble in water—  
 $\text{Fe}_2\text{O}_3$ ;  $\text{Al}_2\text{O}_3$ ; humus . . 1.5%

*Ammonium Nitrate* is prepared at Notodden and Rjukan by neutralising the 30% nitric acid with pure ammonia liquor ( $\rho$  0.880). The resulting liquid is filtered, evaporated in vacuum pans until it has  $\rho$  1.35, and is then allowed to crystallise. The crystals are centrifuged and dried in a Bühler's apparatus, when they contain 99.9% of  $\text{NH}_4\text{NO}_3$ .

In addition to the Birkeland and Eyde furnace several other types of arc furnace have been

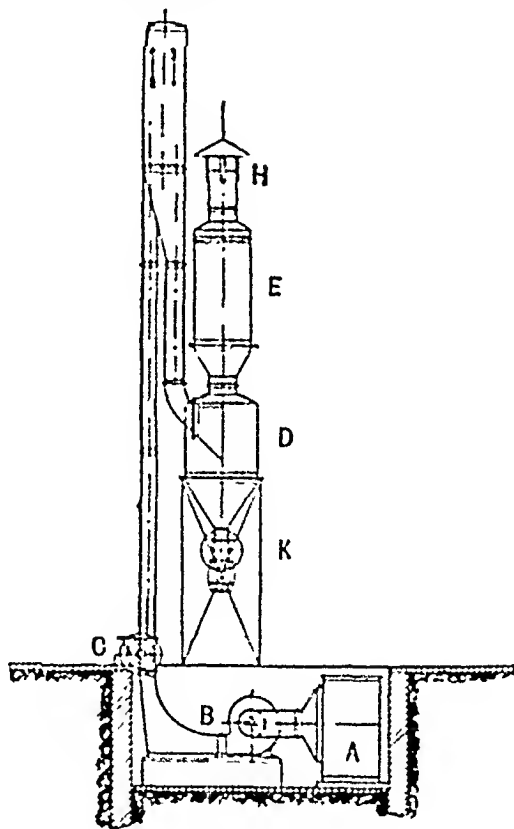


FIG. 3.

in use technically and many others have been proposed which have never been used. The *Schönherr furnace*, devised in 1905 (Trans. Amer. Electrochem. Soc. 1909, 16, 131; Elektrotechn. Z. 1909, 30, 365, 397), which was worked in Norway, and on a limited scale in Germany in 1914-18, consisted of a vertical iron tube (16 ft. or more in diameter) inside which an axial arc flame was burning. The yield in the Schönherr furnace is increased by 115% by using lithium-copper alloy electrodes and oxygen-enriched air (Wakker and Briner, Helv. Chim. Acta, 1936, 19, 320; Briner, Bull. Soc. Chim. 1937, [v], 4, 1325). The *Pauling furnace* (Russ. Z. Elektrochem. 1909, 15, 544; J. W. Mellor, "Comprehensive Treatise of Inorganic and Theoretical Chemistry," Vol. VIII, London, 1928, p. 375)

originally used at Patsch, near Innsbruck, and later at Legnano in Italy, had horn-shaped electrodes between which an arc was struck and then blown into a flame by a rapid current of preheated air from a nozzle below the electrodes.

Small units (500–600 kw. at 5,000 v.) with electrodes very close together at their point of convergence, so that no special device for lighting the arc was necessary, were used, the waste heat being utilised by building the furnace units in steam boilers. The yield is increased from 23 to 25 g. of nitric acid per kw.-hr. to 74.4 g. per kw.-hr. by using special electrodes of aluminium, preferably alloyed with other metals such as barium (Rossi, B.P. 23959, 1913). Finely divided iron oxide carried off from iron electrodes acts catalytically in decomposing nitric oxide in the hot arc gas.

The *Moscicki furnace* (B.P. 20497, 1903), used at Chippis in Switzerland, had an arc caused to revolve in the space between two concentric electrodes by a magnetic field, and a special absorption apparatus was used. The *Nitrum process*, developed by the Société Nitrum of Zurich (Gros, *Compt. rend.* 1920, 170, 811), and used for a time at Bodio in Switzerland and Merseburg in Germany, used a dry mixture of equal volumes of oxygen and nitrogen circulated in a closed system, the oxides of nitrogen (after addition of oxygen) being condensed by cooling or absorbed in water cooled at 0°; the furnace was filled with flame, the gas being blown in tangentially, and the flame suddenly chilled by passing through a water-cooled tube. The yield was stated to be 70–75 g. of nitric acid as 62% acid per kw.-hr.

The *Scott* (J.S.C.I. 1917, 36, 771) and *Island* (U.S.P. 1316445 and 1317705, 1919) are furnaces do not seem to have been in technical use.

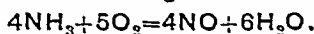
**The Häusser Process.**—The formation of nitric acid when a mixture of oxygen and hydrogen containing some nitrogen is burned was noted by Cavendish in 1784 (p. 557b). Kolbe (*Annalen*, 1861, 119, 176) found that oxides of nitrogen and nitric acid are formed when a jet of hydrogen burns in oxygen containing some nitrogen, and he suggested that the reaction might be used technically. An increased yield in the explosion reaction at higher pressure was discovered by Hempel (*Ber.* 1890, 23, 1455). Nitrogen peroxide is also formed by burning carbon monoxide in air under pressure (Haber and Koenig, *Z. Elektrochem.* 1910, 16, 18) and many proposals have been made to bring about the union of atmospheric nitrogen and oxygen by the combustion of various fuels (T. H. Norton, "The Utilisation of Atmospheric Nitrogen," Dept. of Commerce, Washington, 1912). The yield is always small and the oxides of nitrogen are mixed with large volumes of the products of combustion, so that all such processes are very unpromising.

Häusser (*Chem. Trade J.* 1914, 55, 46, 69; *Stahl und Eisen*, 1921, 41, 956, 999; J.S.C.I. 1922, 41, 253n; Nöh, G.P. 306451, 1916; Görlinger, G.P. 316253, 1919; a careful discussion is given in the Nitrogen Products Committee "Report." H.M. Stationery Office, 1919, pp. 277–285) proposed to explode a mixture of air and a combustible gas, such as coal gas or

coke-oven gas under pressure in a gas-engine cylinder or a bomb, when a gas containing 0.3–0.6% by volume of nitric oxide is formed. An oil spray may also be used. Trials on a small scale pointed to a yield of 135 g. of nitric acid per cu. m. of fuel gas of calorific value of 483 B.Th.U. per cu. ft., with an initial compression of 3–2 atm. and a pre-heat of 240°. Enriching the air with oxygen should increase the yield. The process of Bender (G.P. 192883, 1906; 217079, 1908) was to work at atmospheric pressure, and Brunler (*Chem. Age*, 1926, 14, 29; cf. Seniscle, J.S.C.I. 1930, 49, 63r) proposed to burn a submerged flame of gas, oil, or powdered fuel under lime water to form calcium nitrate.

#### THE OXIDATION OF AMMONIA.

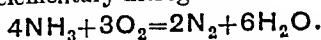
In 1788 the Rev. I. Milner (*Phil. Trans.* 1789, 79, 300) found that ammonia gas is oxidised to nitric oxide when passed over heated manganese dioxide, and J. Black ("Lectures on Chemistry," 1803, pp. 245, 455; Partington, *Nature*, 1922, 109, 137) states that the process was used in France on the large scale during the Napoleonic wars for the manufacture of saltpetre. This observation was followed by the better known researches of Prof. Frédéric Kuhlmann, of Lille, who (*Mém. Soc. Sci. Lille*, 1938, 15, 88; *Annalen*, 1830, 29, 272) observed that when a mixture of ammonia and air is passed over platinum sponge heated to about 300° the platinum continues to glow and oxides of nitrogen are formed:



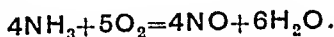
A slight reaction only was noticed when the gas was passed through an empty heated porcelain tube. Kuhlmann also found that platinum black is less efficient than platinum sponge, and copper, nickel, iron, and copper hydroxide are still less active; he also found that cyanogen and hydrocyanic acid are very readily oxidised—an observation confirmed by Moldenhauer and Wehrheim (*Z. angew. Chem.* 1914, 27, 334). Krant (*Annalen*, 1865, 136, 69) noticed that red fumes, with intermittent explosions, result when a hot platinum spiral is hung in a flask containing ammonia solution through which a current of oxygen is passed. The formation of ammonium nitrite and nitrate on passing ammonia and air over platinised asbestos heated to redness was described by Warren (*Chem. News*, 1891, 63, 290). The yield of oxides of nitrogen with platinised asbestos as catalyst was investigated by Schmidt and Böcker (*Ber.* 1906, 39, 1366). Platinised glazed porcelain (Schick, B.P. 13954, 1907) is said to have a longer life than platinum sponge (Taliani, *Giorn. Chim. Ind. Appl.* 1921, 3, 408). Platinised puzzolana has been used (Marnier, *Chem. Trade J.* 1935, 97, 82), also platinum and platinum-rhodium splintered on porcelain (Klevke, *J. Chem. Ind. Russ.* 1937, 14, 98).

The conditions for obtaining a practical yield with platinum were investigated by Ostwald and Brauer (*Z. Elektrochem.* 1903, 9, 485; the method is described in B.P. 698, 8300, 1902, and 7909, 1908; a German patent was not granted on account of the prior work of Kuhlmann). It was found that the gas must pass rapidly over

the catalyst, otherwise the ammonia is largely burnt to elementary nitrogen:



Under suitable conditions, however, well over 90% of the ammonia may be oxidised to nitric oxide:



Nitric oxide is the first ascertainable product of the oxidation. The reaction begins at about 550° and proceeds rapidly and practically completely at 650–800°. The yield in good working is 95–97% and usually averages 90–92%. The reaction proceeds equally well with dry or moist gases; a little moisture seems to be slightly beneficial.

A technical plant based on Ostwald's investigations was erected in 1909 at the works of the Lothringian Colliery Co. at Gerthe, near Bochum, which produced more than 1,800 tons of ammonium nitrate per annum (Chem. Trade J. 1915, 56, 553). The patents were taken over by the Nitrogen Products Co., who erected factories at Vilvordo in Belgium and Dagenham in England.

The process in the Ostwald form was largely used in France during 1914–18, the ammonia being derived from cyanamide. The works were installed at Angoulême and Bassens, and a full description of them was given in the Third Edition of this "Dictionary" (1922, Vol. IV, p. 596).

The Ostwald converter consists of two vertical concentric tubes, acting as a heat exchanger. The heat is transmitted through the walls of the inner tube to the mixture of air and ammonia, which passes up the annular space between the tubes to the catalyst, which is placed at the top of the inner tube, and the hot oxidised gas passes down inside this. The temperature of the catalyst is maintained at 800–830° without external heating. The external tube is of iron, enamelled inside, the inner tube of nickel, 3.5 m. long, 63 mm. in diameter, and 1 mm. thick. The iron tube is 100 mm. in internal diameter and is only 3.25 m. long, so that the nickel tube protrudes 25 cm. below. This is prolonged by an aluminium tube, in which the gas cools to 260–270° before passing into a large aluminium main collecting the products of several converters. The iron tube is lagged outside to hinder radiation.

The catalyst is prepared by taking two strips of platinum foil, 2 cm. wide and 0.01 mm. thick, crinkling one into ridges 1 mm. apart, laying this on the other flat strip, and rolling the two into a circular pad 65 mm. in diameter, weighing 50 g. At the top of the nickel tube and inside it are lugs, on which the roll of platinum rests. The outer iron tube is closed at the top by a hinged lid, with a mica inspection window. The activity of the platinum increases rapidly with use for some hours. It then slowly falls off and the catalyst requires renewal after three months. The activation of the platinum depends on a peculiar physical change (E. K. Rideal and H. S. Taylor, "Catalysis," Macmillan, 1919, p. 97); the metal swells into microscopic efflorescences, probably owing to solution of gas and subsequent expulsion.

Each Ostwald converter unit produced 100 kg. of nitric acid per 24 hours. The mixture of air and ammonia contained about 8.5% of ammonia by volume. Before passing to the converter the two gases should be thoroughly mixed. The gas should also be filtered from dust, since iron oxide acts very prejudicially on the catalyst.

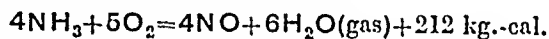
The use of a single layer of electrically heated platinum gauze as a catalyst was described by Frank and Caro (Schuphaus, Metall und Erz, 1916, 13, 21) and by Landis (U.S.P. 1193796 to 1193800, 1916; Chem. Met. Eng. 1919, 20, 470; on the construction of catalysts, see "Oxidation of Ammonia," Munitions Inventions Department, H.M. Stationery Office, 1919; and Campbell, J. Ind. Eng. Chem. 1919, 11, 468).

The basis of all recent improvements is to be found in the patent of Kaiser (B.P. 20325, 1910 conv. 1909; 24035, 1911 conv. 1910; G.P. 271517, 1909), who proposed the use of several superposed fine platinum or iridium gauzes in close contact, the mixture of air and ammonia gas being preheated to 300–400° before passing to the catalyst. In this way a very rapid stream of gas may be passed and the output correspondingly increased.

Kaiser claimed that some atmospheric nitrogen was oxidised along with the ammonia, but this has not been confirmed and was probably based on faulty analytical control.

In March, 1917, Partington and Parker used two platinum gauzes separated by thin silica rods, the lower gauze being electrically heated. Although separated gauzes are slightly more efficient than gauzes in contact (Perley and Smith, J. Ind. Eng. Chem. 1920, 12, 5, 119; Chem. Met. Eng. 1920, 22, 125) they tend to warp in use, and multiple gauzes in contact, generally stitched together with the same kind of wire, are generally used. Two layers of gauze give as good results as three or more (Perley and Smith, *l.c.*; Titlestad and Spangler, U.S.P. 1927508, 1933).

The yield is best with a suitably rapid rate of flow of gas through the gauze and a suitable gauze temperature, but is not very sensitive to these conditions (on the velocity of oxidation, see Borskov, J. Appl. Chem. Russia, 1932, 5, 163). The gauze temperature is most easily measured by means of an optical pyrometer through a suitable inspection window of quartz or clear mica (shown at *a* in Fig. 4). The observed temperatures must be suitably corrected to black-body temperatures, the difference being 50–100°; a table of corrections is given by Perley and Smith (*l.c.*). Although the gauze is maintained automatically at a dull red-heat by the exothermic reaction:



the yield is only about 85% unless the gauze is electrically heated or the gases preheated, when it reaches about 95%. The temperature of preheating of the gas may be about 600° as a maximum (Perley and Smith, *l.c.*).

The yield is dependant on the gas composition; more oxygen than is required to form NO should always be present in the air-ammonia mixture: the best mixture is one which corresponds theoretically to the formation



of  $\text{N}_2\text{O}_3$  (J. R. Partington and L. H. Parker, "The Nitrogen Industry," Constable, 1922, p. 293). According to Perley and Smith (*loc. cit.*) the ammonia content should not exceed 11% by volume with a flow velocity of 1.827 l. per min. of intake gas per sq. cm. of catalyst. A ratio  $\text{O}_2:\text{NH}_3$  lower than 0.75 gives practically only nitrogen; above 1.25 nitric oxide is almost the sole product (cf. Maliarevski, *Z. angew. Chem.* 1925, 38, 1113; Andrussov, *ibid.* 1926, 39, 321; 1927, 40, 166; Uchida, *J. Physical Chem.* 1926, 30, 1297; Adadurov, *J. Chem. Ind. Moscow*, 1933, 10, No. 2, 37; *Khimistroi*, 1933, 5, 2285; Epstein,

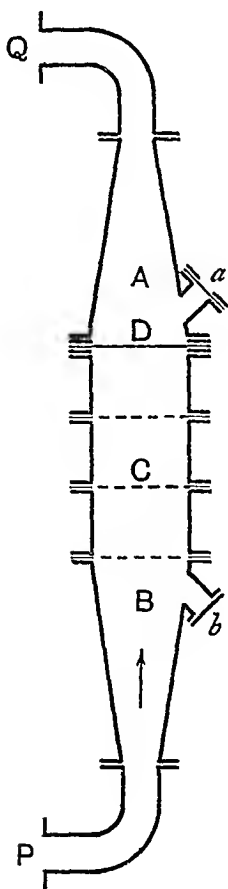


FIG. 4.

Manuring and Harvest (Russ.), 1930, Nos. 9-10, 749; 1931, No. 1, 75; Hennel, *Przemysl Chem.* 1932, 16, 258; Wein, *ibid.* 1933, 17, 75).

Since the reaction is very rapid, a high flow rate is used and the apparatus ("converter") for oxidation is correspondingly small. A cross-section of 4 in. by 6 in. with two gauzes suffices for a technical unit capable of supplying oxides of nitrogen for a large sulphuric acid chamber plant, and converters with 2 in. by 3 in. gauzes function very satisfactory. In making nitric acid catalyst cross-sections of 1 or 2 sq. ft. or more are used, but if too large there is a tendency for the gauzes to sag. An output of 1.5 tons of nitric acid per 24 hours per sq. ft. of double

gauze, which corresponds with 16 kg. of nitric acid per g. of platinum per 24 hours, is normal (J. R. Partington, *J.S.C.I.* 1918, 37, 337R; "The Oxidation of Ammonia Applied to Vitriol Chamber Plants," H.M. Stationery Office, 1919).

The form and material of construction of the converter may be varied considerably. Upward, downward, or sideways, flow of gas through the gauze may be used indifferently; the material is limited by the circumstance that iron oxide is a powerful catalyst poison.

The standard type of converter designed by the author (Fig. 4) consists of top and bottom cones A and B, with rectangular body pieces C between, all in cast aluminium  $\frac{1}{8}$  in. thick. Three body pieces are shown, but two, or even one, may suffice. The area inside is 4 in. by 6 in. The pieces are provided with flanges,  $\frac{3}{4}$  in. wide, to facilitate bolting together, and perforated baffles of sheet aluminium are inserted between the body pieces, except at the junction between the top cone and body piece, which is occupied by a catalyst D of two layers of platinum gauze, of pure platinum wire 0.0025 in. diameter, woven in uniform mesh with 80 strands to the linear inch.

The gauzes are conveniently stitched together with some of the same wire, and the double gauze is supported between two flat aluminium plates cut out in apertures about  $\frac{1}{8}$  in. smaller than the gauze dimensions, and with asbestos-paper packing extending to the inner edge of the apertures, the plates being suitably screwed together. The catalyst unit is thus detachable and can be removed and replaced at will. Before fitting into the frame, the gauze is boiled for a few minutes with concentrated hydrochloric acid, washed in a porcelain photographic developing dish with distilled water, and dried on clean filter paper. On no account must the gauze be touched with dirty fingers during fitting, and the catalyst units must be stored in a perfectly clean wood box to preserve them from dust. The fitting should be carried out in a room free from dust and not in a workshop where iron is manipulated. Inlet (p) and outlet (q) elbows of cast aluminium are bolted on the cones B and A, respectively.

The converter is started by passing a slow stream of ammonia-air mixture and heating the gauze by a hydrogen flame inserted through the aperture a, which is afterwards closed by a bolted-on aluminium plate. It is desirable to take out the platinum gauzes once every two or three months, and clean them by boiling with concentrated hydrochloric acid. After six or eight months' use the platinum begins to disintegrate, and is replaced by a new gauze. Perfectly new gauze is not very active, but rapidly becomes activated after a day's use. Activated gauzes may be stored ready for use.

Although platinum is said to evaporate slowly even at 580° (Uchida, *J. Physical Chem.* 1926, 30, 1297), it is claimed that the loss of platinum is due solely to fine particles carried off by the gas-stream from the cauliflower-like excrescences (see E. K. Rideal and H. S. Taylor, "Catalysis," Macmillan, 1919, p. 97) which develop on the wires, and may increase their diameter by 12μ. (Figurovski, *J. Appl. Chem. Russia*, 1938, 11,



1440). The loss amounts to about 0.003 oz. troy per ton of nitric acid with normal working (Imison and Russell, J.S.C.I. 1922, 41, 37r; cf. Kulikov, J. Chem. Ind. Russ. 1937, 24, 1683; Adadurov and Grigoriev, J. Appl. Chem. Russia, 1937, 10, 1548; Epshtein and Tkatschenko, *ibid.* 1938, 11, 733). The loss from Pt-Rh gauzes is said to be only about half that from pure Pt (Handforth, Ind. Eng. Chem. 1931, 23, 860).

Preliminary prolonged heating in hydrogen increases the activity of the platinum (Adadurov and Didenko, J. Appl. Chem. Russia, 1934, 7, 1339). On the other hand, the superior activity and stability of a ternary alloy catalyst (Pt 92, Rh 5, W 3%) are ascribed to its low power of dissolving hydrogen (Adadurov and Pevni, J. Phys. Chem. Russ. 1937, 9, 592).

Heating alloys of platinum metals (e.g., platinum with 2% of ruthenium, but not platinum-rhodium) above 900° until crystal growth is detected by X-rays is said to enhance their activity (I.G. Farbenind. A.-G., B.P. 489306, 491143, 1937; Ruthardt, *Angew. Chem.* 1938, 51, 760).

Gauze consisting of platinum with 10% of rhodium is now used (Chem. Trade J. 1931, 88, 584; Barmag Meguin A.-G., B.P. 334466, 1929; Du Pont de Nemours, B.P. 306382, 1928). Platinum net covered with finely divided rhodium has also been proposed (I.G. Farbenind. A.-G., B.P. 331728, 1929). An alloy of 9 parts of platinum and 1 part of rhodium is best (Handforth and Tilley, Ind. Eng. Chem. 1934, 26, 1287). According to Decarrière (Bull. Soc. chim. 1925, [iv], 37, 412), platinum-palladium alloy is better than platinum; iridium (recommended by Parsons, J. Ind. Eng. Chem. 1919, 11, 541) is decidedly inferior (Duparc, Wenger, and Urfer, *Helv. Chim. Acta*, 1928, 11, 337); palladium is less efficient than platinum except at high ammonia concentrations (Decarrière, Bull. Soc. chim. 1924, [iv], 35, 48). The use of various forms of platinum has been investigated (Pascal and Decarrière, *Mém. Poudres*, 1924, 21, 68, 87; Taylor, *Chem. Met. Eng.* 1920, 26, 1217; Curtis, *ibid.* 1922, 27, 699; Campbell, J. Ind. Eng. Chem. 1919, 11, 468). Platinum alloyed with 1% of tantalum or 2% of tungsten (I.G. Farbenind. A.-G., F.P. 716516, 1931), and chips of an alloy of platinum, rhodium, and tungsten (Du Pont de Nemours, U.S.P. 1978198, 1934), have been proposed. Gauze with pure platinum warp and platinum-rhodium woof is proposed (Taylor and Grasselli Chem. Co., U.S.P. 1927963, 1933). Alloys of platinum with 3% of cobalt or 3% of tungsten, and the ternary alloy of Pt 92, Rh 5, and W 3%, are all more active than platinum, and the last has great stability (Adadurov and Pevni, J. Phys. Chem. Russ. 1937, 9, 592). The use of platinum-rhodium alloy is said to be attended with greater difficulty in starting and greater sensitiveness to working conditions than that of pure platinum. The presence of 3% of tungsten in the platinum gauze is said to make it twice as active as ordinary platinum at 750° (Adadurov and Atroschenko, J. Appl. Chem. Russia, 1936, 9, 1221).

Parsons and Jones (B.P. 132551, 1918; Ind.

*Eng. Chem.* 1919, 11, 541; 1927, 19, 789; Taylor, *ibid.* 1927, 19, 1250; Perley and Varrell, *ibid.* 1929, 21, 222) use 4 layers of platinum gauze, of 0.0026 in. diameter and 80 mesh, in close contact, formed into a cylinder closed at the bottom with a silica plate. The cylinder hangs inside a chamber lined with glazed bricks and no preheating of the gases is used, the heat radiated from the gauze and walls of the chamber sufficing. The efficiency was 90-91% with an output of 70 lb. of ammonia oxidised per oz. of platinum per 24 hours. The efficiency was improved to 95% and the output to 100 lb. of ammonia oxidised per oz. of platinum per 24 hours by preheating the gas to 600°C. by mixing preheated air with ammonia gas in an iron pipe lined with silica (Perley, *Chem. Met. Eng.* 1920, 22, 125; Ind. Eng. Chem. 1920, 12, 5, 119). Parsons recommended preheating the gas and operating the gauze at 1,000°, but this temperature is much too high and causes loss of platinum. The production, however, with this type of converter is said to be twice as high at 925-950° as at 725°, and the efficiency 95% as compared with 88-90% at 725° (Kaltenbach, *Chim. et Ind.* 1929, 21, 701). Owing to the weight supported by the gauze cylinder, the wire must be thicker than that used with flat gauzes, and since the supposed benefit of the radiant heat is illusory (gases being transparent to radiant heat), the advantage a cylindrical gauze has over a flat one is not obvious.

Enamelled iron converters, made by the Cannon Iron Foundries, Deepfields, Staffs., are said to be very satisfactory.

Imison and Russell (J.S.C.I. 1922, 41, 37r) describe a converter of iron, protected with enamel or by painting with sodium silicate solution and barium sulphate, which utilises the heat of reaction in preheating the gas. Chromium steel or chromium plating withstands oxides of nitrogen at 200° (Thompson, *Trans. Amer. Electrochem. Soc.* 1926, 50, 101).

An apparatus for producing the air-ammonia mixture (1 vol. of ammonia to 7.5 vol. of air) by passing air through 25% ammonia solution in a packed tower (Fig. 5) and driving off the ammonia by steam admitted at the base of the tower is described by Imison and Russell (*l.c.*) (Richardson, U.S.P. 2119721, 1938; Chemical Construction Co., U.S.P. 1748646, 1930, uses the heat of the oxidised gas to drive off ammonia from a solution in a tower).

Before entering the converter the gas is filtered through glass wool, as even traces of oxide of iron, present in dust, poison the platinum catalyst.

Oxides of nitrogen from ammonia oxidation provide a convenient source for use in sulphuric acid chamber plants, the gas being introduced at a suitable point, say after the Glover tower (Schuphaus, *Metall und Erz*, 1916, 13, 21; "The Oxidation of Ammonia applied to Vitriol Chamber Plants," Munitions Inventions Department, H.M. Stationery Office, 1919; Chem. Trade J. 1931, 88, 584; Spangler, *Chem. and Met. Eng.* 1928, 35, 342; Kieffler, Ind. Eng. Chem. 1927, 19, 1153). The high toxicity of oxides of nitrogen must be kept in mind (Chem. Trade J. 1933, 93, 281).

The analytical control of ammonia oxidation plant is described by Whittaker *et al.* (Ind. Eng. Chem. [Anal.], 1930, 2, 15; E. Berl and G. Lunge, "Chem.-tech. Untersuchungsmethoden," Berlin, 1932, II, i, 573, 576).

The effects of impurities in the ammonia have been investigated. Perley (J. Ind. Eng. Chem. 1920, 12, 5, 119) states that very small amounts of phosphine (2-3 p.p.m.) are detrimental; this impurity, which may be present in cyanamide ammonia, may be removed (Parsons and Jones,

B.P. 136342, 1919) by passing the mixture of ammonia and air, heated to 50-60°C., over a catalyst composed of "a metal of the silver group" on a support of carbonised cellulose fibre. Ammonium phosphate is formed, which is retained by the carbon. Taylor and Capps (J. Ind. Eng. Chem. 1918, 10, 457) state that acetylene present to the extent of 0.02% reduces the yield from 95% to 89%, and 0.1% to 65%. The effect of acetylene is probably due to phosphine present as impurity. Decarrière (Compt.

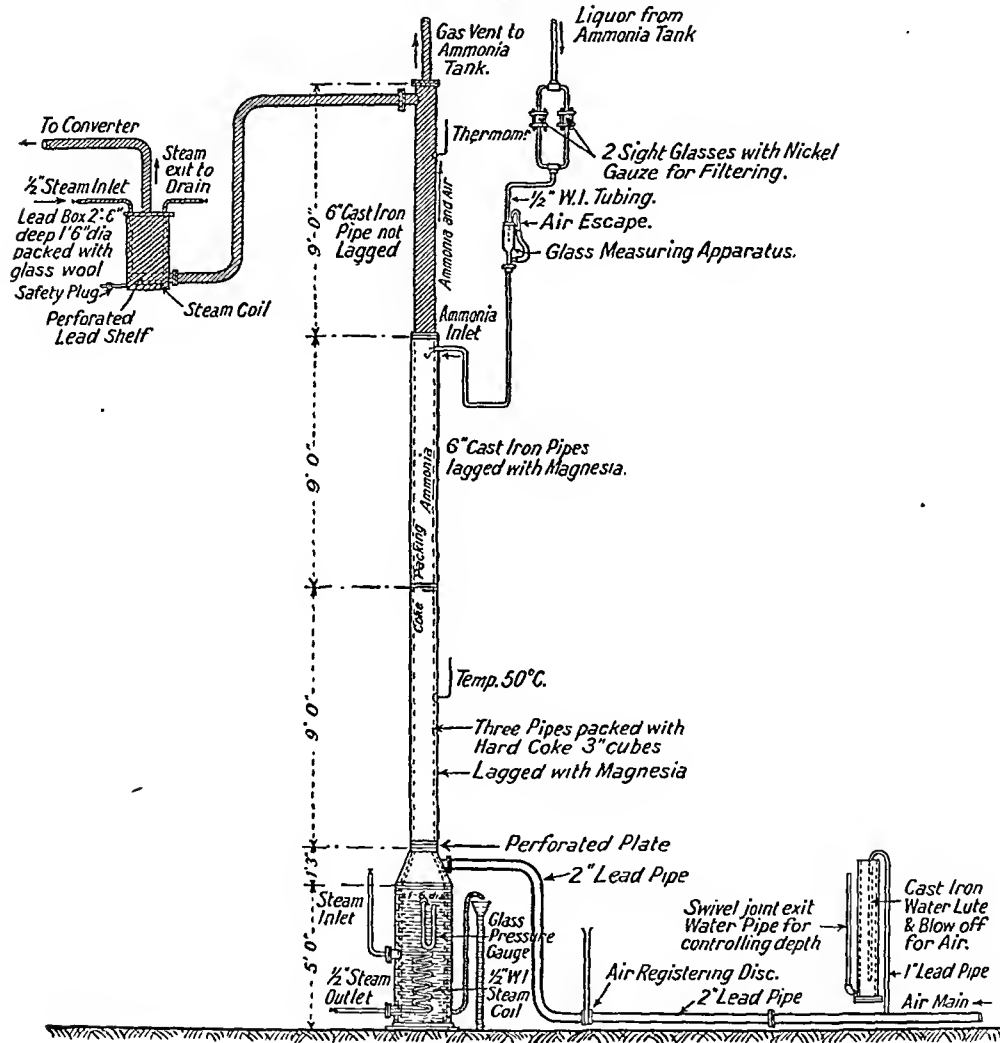


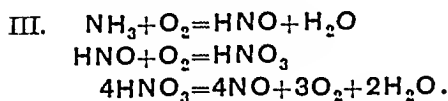
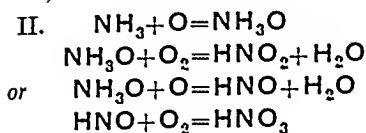
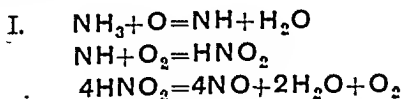
FIG. 5.

rend. 1921, 172, 1663; 173, 148; 1922, 174, 460, 756) finds that small amounts of hydrogen (0.44% by vol.) slightly increase the activity of the platinum catalyst, but larger amounts (1.0-1.5%) slightly reduce it. Hydrogen sulphide lowers the activity, the effect depending on the concentration rather than on the total amount which has passed over the catalyst. Decarrière found that acetylene causes a slight increase in the yield for the first few minutes, followed by a fall which is proportional to the absolute amount of impurity which has passed rather

than to the concentration, and continues even when pure gases are then used. Later work (Pascal and Decarrière, Mém. Poudres, 1924, 21, 1, 87; Yee and Emmett, Ind. Eng. Chem. 1931, 23, 1090) showed that up to 0.4% of pure acetylene has no effect but 0.02 p.p.m. of phosphine has a poisoning influence and 0.2 p.p.m. definitely injures the platinum. The addition of 0.07% of hydrogen sulphide protects the platinum from phosphine and also gives a 3-4% increase of efficiency with unpoisoned platinum. Pyridine up to 2% in ammoniacal liquor can be

tolerated, but the life of the platinum is shortened (Chem. Trade J. 1931, 88, 584). Lead tetraethyl is a powerful catalyst poison.

Many theories of the mechanism of ammonia oxidation have been proposed (see Gmelin's "Handbuch der anorganischen Chemie," Berlin, 1936, Part 4, p. 655). The reaction probably occurs on a platinum surface covered with atomic oxygen, and several alternative intermediate products are possible (cf. Bodenstein, Z. Elektrochem. 1930, 36, 756; Krauss and Schuleit, Z. physikal. Chem. 1938, B, 39, 83; 1939, B, 45, 1), e.g.,



The nitrous oxide formed in abnormal conditions (Nagel, Z. Elektrochem. 1930, 36, 754; I.G. Farbenind. A.-G., B.P. 325475, 1928) may be derived from HNO:



Hydrazine may also be formed in abnormal conditions (Hofmann and Korpiun, Ber. 1929, 62 [B], 3,000; Koenig and Wagner, Z. physikal. Chem. 1929, 144, 213).

The ammonia oxidation plant of the Höchst Farbwerke (vormals Meister, Lucius, und Brüning), with a capacity of 140,000 tons of nitric acid per annum, is of a type commonly used in works making ammonia by the Haber-Bosch process (Partington, J.S.C.I. 1921, 40, 185R).

The ammonia liquor (about 25% ammonia) is stored in four overhead spherical steel tanks, each of 264,200 gallons capacity. The liquor is rectified in four stills, one spare, of the Savalle type with 15 effects, each with a capacity of 20 tons of ammonia daily. The gas not used for oxidation is absorbed in a plate tower 30–40 ft. high. Ammonia from gas liquor is scrubbed with caustic soda solution of 48–53° Tw. and then passed through charcoal purifiers in the usual way to remove sulphur compounds. The ammonia gas from the stills is freed from moisture by refrigeration with ice-cold water; the presence of moisture causes scaling of the iron pipes and is also believed to be prejudicial to the conversion, although this is probably incorrect.

The ammonia gas and air are metered through Venturi meters and driven by ten 55-kw. centrifugal blowers to the filters and converters. The mixture contains 12.5% by volume of ammonia, regulated within narrow limits. The ammonia supply pipe is 6 in. in diameter and the air pipe 18 in. in diameter. The air is filtered through cloths in a wooden box and the mixed gas carefully filtered from dust and ammonium

salt fumes through eight layers of linen cloth in chambers 9 ft. by 5 ft.

The gas passes under 6 in. water pressure through two central mains in the converter house, from which it is diverted to the 224 converters, each provided with a circular platinum gauze catalyst of 20 in. diameter, or 2.12 sq. ft. cross-section. The maximum output of each converter is 1.5 tons of nitric acid per 24 hours, the efficiency of oxidation being 89%. The efficiency from ammonia to dilute acid (including the efficiency of the absorption plant) is 87%, that from ammonia to strong acid (including the concentrating plant) is 84%.

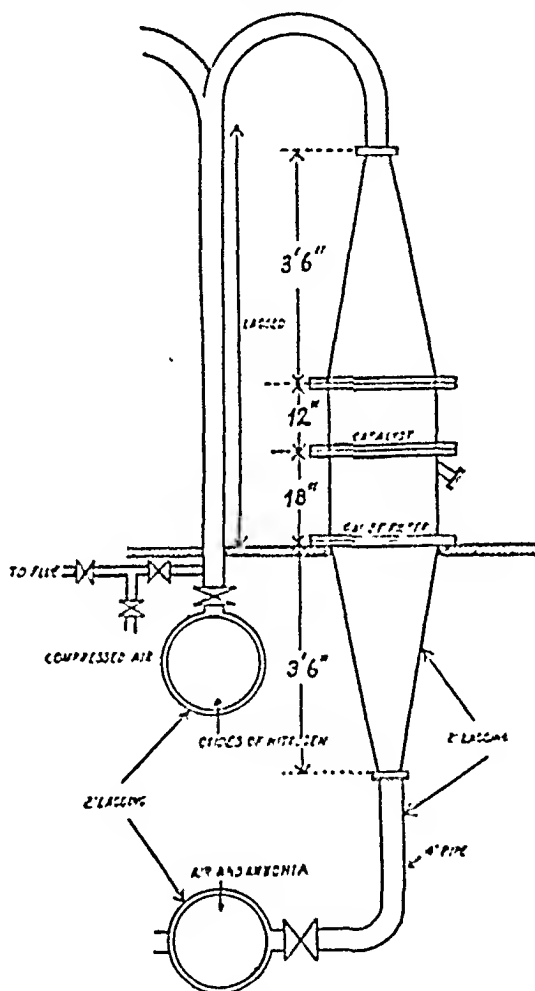


FIG. 6.

The body of the converter (Fig. 6) is of cast iron, in four sections with flanges. The two middle sections, 18 in. and 12 in. high, support the catalyst between them; the conical top and bottom pieces are each 3 ft. 6 in. high. The top cone is lined with sheet nickel to protect it from the hot gas. The catalyst, clamped between asbestos rings, is started by heating to redness by a hydrogen or coal-gas flame inserted below it through a lighting hole shown in the figure.

The exact construction of the catalyst has been differently stated. It consists of 2, 3, or 4 platinum gauzes, of 20 in. diameter, of 0.06-mm. wire with 80 meshes to the linear inch. The

gauzes are possibly spot-welded, and are supported on a grid of ten stout platinum wires, 1 mm. in diameter, spaced at 10 cm. distance, and probably two gauzes are used.

The converters are arranged in two sets of seven or eight on each side of separate inlet and outlet mains, the latter 1 ft. in diameter and connected with the converters by 4-in. pipes, lagged outside with diatomite brick shaped to fit, cemented and wired. The upper bend pipe of the converter is not lagged, so as to allow for expansion. Before entering the converters the gas passes from a common main to a vertical, lagged, multitubular preheater, 15 ft. by 5 ft. external dimensions, in which it is heated by steam. The purpose of this is to prevent condensation of acid from the hot gas coming from the converter when it passes through the heat exchanger, which is identical in dimensions with the preheater. In it the warmed gas passes in counter-current to the gas from the converters, and leaves at 200°C. Two heaters so arranged serve 14 converters. The temperature of the

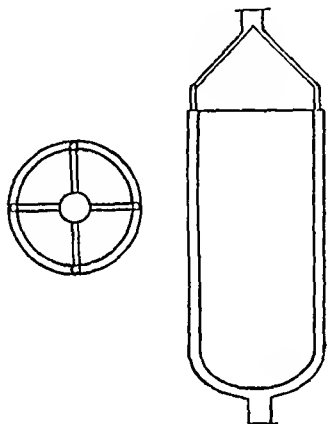


Fig. 7.

catalyst is about 800°; the gas leaves the converter at 650–700°. In starting the converters extra air can be added and the only partly converted exit gas by-passed to a chimney until the gauze is activated. Gate valves are used, with a slight air pressure on the side of the valve not in contact with the gas to prevent leakage. In 56 of the later type of converters, the gas passes by a lagged 3-ft. main through two tubular boilers, leaving these at 270° to the heat exchanger. In this way four tons of water are evaporated per hour, and the steam is used for warming the gas, as described above. One to three men only are necessary to look after all the converters.

The gas containing nitric oxide and steam coming from the converters passes through eight cast-iron mains 18 in. in diameter, supported on three ferro-concrete bridges, to four rows of eight absorption towers. Each row of towers is provided with twelve intensive coolers of special design, i.e., 48 coolers in all. These coolers (Fig. 7) are of aluminium, with an annular space between the outer wall and an inner vessel, the gas entering above through four inlets.

In these coolers much of the steam in the con-

verter gas condenses to water, and, since the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  requires time (see p. 520a) hardly any nitric oxide is oxidised at this stage. This separation of water by cooling before the gas enters the absorption system is an important feature of all modern ammonia oxidation processes (Partington and Rideal, B.P. 131942, 1918; J. R. Partington and L. H. Parker, "The Nitrogen Industry," Constable, 1922, p. 288; Triggs, B.P. 336233, 1929; Frischer, B.P. 363436, 1929; Frank and Caro, B.P. 337847, 1929; F.P. 748365, 1932). The gas may be further dried by sulphuric acid (Partington and Parker, *op. cit.*, p. 294; I.G. Farbenind. A.-G., B.P. 284839, 1927; Kartachev and Zeitlin, Ukrain. Chem. J. 1930, 5, 257). Cooling in a tower with water-cooled aluminium helices (Krase, Chem. and Met. Eng. 1926, 33, 674), which removes less than 1% of oxides of nitrogen, may be used, and other methods, such as the use of silica gel, for removal of residual water vapour could be used in cases where the converter gas is to be treated otherwise than by water absorption (see p. 576a).

The weak acid condensate from the coolers at Höchst is put down the fifth absorption tower in a set of eight. The gas leaves the coolers at 30° through four pottery mains 1 ft. in diameter, joining to a single brick chamber at the base of each set of eight towers attached to 56 converters. Secondary air necessary for conversion of nitric oxide to nitric acid in the towers is admitted at this point, as any unnecessary excess of oxygen must be avoided in the coolers.

The towers are 41 ft. high and 21 ft. in diameter internally. The walls comprise three layers of brickwork, the outer layer of bricks 6 by 4 in., set in a mixture of sodium silicate and kieselguhr. The top of the tower is slightly domed, and there is a central partition in each tower, the gas passing up one side and down the other, and then going to the next tower through a brick channel at the base. The towers are packed with stoneware rings. The total internal volume of all the towers is 35,320 cu. ft., which amounts to only 81 cu. ft. per lb. of  $\text{NO}_2$  absorbed per minute, as compared with 1,500 cu. ft. as used at the French works at Bassens.

The result of this small tower capacity is clear when it is found that at Höchst no less than 25% of the oxides are absorbed as nitrate by saturated sodium carbonate solution fed to the last two towers. The liquid in the first of these towers is allowed to become acid, so that the nitrite is converted into nitrate, whilst that in the second is kept alkaline, to absorb the oxides of nitrogen driven out of the first when conversion into nitrate occurs (see p. 574b; Partington and Rideal, B.P. 131942, 1918). The solution of nitrate is evaporated by the waste heat of the converters. The remaining towers are fed with water for the production of nitric acid. The efficiency of the absorption plant is 97%. Acid of 50% strength is obtained from the first tower of the series, the liquid being circulated in the towers by 8-in. chrome-steel centrifugal pumps, each fed by a 3–4-in. pottery main and delivering through a silicon-iron pipe of the same diameter to the top of the tower, two

delivery pipes being used to each tower. The metal pipes are coned and fitted in the same way as the pottery pipes. Acid distribution is effected at the top of the tower by a revolving ribbed disc, turned by a gear shaft at 80 r.p.m.

The acid from the towers passes to the coolers, consisting of S-pipes of silicon-iron cooled externally with water. There are also inter-coolers between each pair of towers except the last, the temperature being kept as low as possible, 25°C. in winter and 40°C. in summer. In summer iced water is used in the coolers. Large stoneware receivers placed above the coolers serve as acid reservoirs. The circulation in each tower is 110 gallons per minute; the loss of acid in the whole system does not exceed 2%.

Twelve stock tanks of brickwork, each holding 1,412 cu. ft., receive the tower acid, from the receivers at the base of the towers, through tapered pottery pipes. No fan is used with the towers.

The tower acid is concentrated by mixing 1 part of 50% acid with 7 parts of sulphuric acid, in five mixing vessels with mechanical stirrers, and then denitrating. About 42,000 tons of sulphuric acid are used per month, but practically all is recovered. (In France, 2.5-3 parts of sulphuric acid only were used, but the nitric acid obtained was of 85% strength, as compared with a more concentrated acid obtained at Höchst.) The nitric acid is recovered partly in two rows of nine silicon-iron towers, 4 ft. in diameter and 25 ft. high, and partly in stone towers, with cast-iron pipe jackets, 35 ft. high and 3 ft. 6 in. in external diameter, the walls being 9 in. thick. Steam at 150°C. is introduced at the base by a 1-in. lead pipe just above the exit for the denitrated acid. The nitric acid vapour from the top of the denitrator passes to a cooler of S-shaped silicon-iron pipes. The acid to be denitrated enters half-way down the cooler, and acid from stock is sent down the upper part to assist condensation. Oxides of nitrogen are removed from the nitric acid by a current of air and recovered in twenty absorption towers. The completely denitrated sulphuric acid is cooled in a water-cooled cast-iron cooler and collected in a large lead-lined tank of artificial stone. It contains about 70% of sulphuric acid, and is reconcentrated in a Kessler apparatus or in Hoenig's modified Pauling apparatus (*Z. angew. Chem.* 1921, 34, 168, 173). The latter is said to be very efficient. (In French practice, a denitrating column 20 ft. high and 18 in. in internal diameter produced 6-8 tons of nitric acid per day with an overall yield of 85-87% on the ammonia burnt in the Ostwald type catalysts. The consumption of fuel in reconcentrating the sulphuric acid was 15-20% of the weight of nitric acid produced.)

The ammonia oxidation converters installed at Muscle Shoals are of an obsolete type, but the absorption system is of interest.

The cooled gas at 30° passes to twelve oxidation towers, 15 ft. square, of chemical brickwork, each divided internally by two walls into four compartments. The gas passes up one compartment, over the top of the dividing wall, down the next compartment, up the next compartment, and down the last. The almost fully

oxidised gas now passes to 24 absorption towers, 35 ft. square and 60 ft. high, of brick, divided into four compartments as before. The first tower of each unit of two is half packed with 6-in. spiral stoneware rings and half with 3-in. spiral rings. The second tower is completely packed with 3-in. rings. Water is circulated in counter-current to the gas and 50% acid is recovered from the towers. The acid is pumped by air lifts, each single stage, throwing 50 gallons of acid per minute. One lift is provided for each compartment, or 96 in all with 24 spares (Oliphant, *Chem. Met. Eng.* 1920, 22, 408). To accommodate these lifts are 120 iron wells, 12 in. in diameter and 100 ft. deep. The lifts consist of 3-in. aluminium pipe with silicon-iron flanges. The towers stand in aluminium saucers. (The renewal of these after corrosion must present a difficult problem.) Air at 100 lb. pressure is supplied by a 1-in. pipe, and the acid in each well section is cooled by water flowing in the well. Between the two towers of each unit is an aluminium fan, and after the second tower a similar fan exhausts the residual gas to the free air. The compressed air from the lifts is also discharged into the free air, which must cause considerable loss of oxides of nitrogen and acid spray. The tower acid passes to twelve aluminium weighing tanks on scales, and is discharged to twelve storage tanks of acid-brick and concrete, from which it is run off by a 3-in. aluminium siphon. When operating at full capacity the plant produces 280 tons of nitric acid per day.

Synthetic nitric acid (free from chlorine) may be distributed in aluminium or chromium steel containers (Anon., *J.S.C.I.* 1930, 49, 1040r).

**Catalysts other than Platinum.**—Many catalysts other than platinum or platinum alloys have been proposed and used. Manganese dioxide was first used by Milner in 1788 (p. 562c), and chromium oxide and chromates were proposed at an early date (Aubertin, *B.P.* 1181, 1871; cf. Goold-Adams, Partington, and Rideal, *B.P.* 126716, 1917).

Other catalysts include manganates, permanganates, dichromates, and alkali plumbites (du Motay, *B.P.* 491, 1871; Schwarz, *Dinglers Polytech. J.* 1875, 218, 219), which are fairly efficient but act strongly on containing vessels at the high temperatures required. In all cases, a higher temperature is required than is necessary with platinum, and the catalyst must be in thicker layers. The cheapness of the oxide catalysts, and the fact that they are less susceptible to poisons than platinum, are points in their favour.

Various catalysts, including oxides, were investigated by Menighini (Gazzetta, 1912, 42, i, 126; 1913, 43, i, 81), Roinders and Cats (*Chem. Weekblad*, 1912, 9, 47), Maxted (*J.S.C.I.* 1917, 36, 777), Neumann and Rose (*Z. angew. Chem.* 1920, 33, 41, 51, 845), Scott (*Ind. Eng. Chem.* 1924, 16, 74; Scott and Leach, *ibid.* 1927, 19, 170), and others.

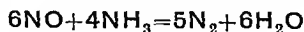
Copper has been proposed as a catalyst (Marston, *B.P.* 19074, 1900) but probably acts only when oxidised, and oxidised nickel has some small catalytic activity. The Farbenfabrik

vorm. F. Bayer (B.P. 18594, 1903) passed ammonia and air at 650–700° over a catalyst of iron oxides and promoters, the Badische Co. using oxides, *e.g.*, of the iron group, in the form of lumps or pieces (B.P. 13687, 1914; 7651 and 13298, 1915). Goold-Adams, Partington, and Rideal (B.P. 126715, 126716, and 135224, 1917) used suitable mixtures of metallic oxides which can be pressed into pastilles or extruded as rods. Oxide of iron promoted by bismuth oxide (Badische Co., B.P. 13848, 1914), tellurium (*idem*, B.P. 13297, 1915), platinum, and lead (*idem*, B.P. 13297 and 13298, 1915); cerium and thorium oxides (Frank and Caro, G.P. 224329, 1907), plumbites of aluminium, zinc, or cadmium (Jones, Morton, and Terziev, U.S.P. 1037261, 1912), lead oxide supported on bone-ash, at 1,000° (Parsons, U.S.P. 1239125, 1917), cobalt oxide and 3% of bismuth oxide (Bray, U.S.P. 1918957, 1933), cobalt vanadate (Ellis, U.S.P. 1558598, 1925), zeolites (Selden Co., B.P. 313153, 1928; Jaeger, U.S.P. 1896627, 1918038, 1926099, 1933), cobalt and aluminium oxides (General Chemical Co., G.P. 350157, 1920) and similar mixed oxide catalysts, have been proposed (*cf.* O. Kausch, "Die Kontaktstoffe der katalytische Herstellung von Schwefelsäure, Ammoniak und Salpetersäure," Halle, 1931, pp. 122 *et seq.*, 185 *et seq.*; S. J. Green, "Industrial Catalysis," Benn, 1928, pp. 130 *et seq.*, 147 *et seq.*; H. A. Curtis, "Fixed Nitrogen," Chemical Catalogue Co., New York, 1932).

A catalyst composed of silica, alumina, chromium oxide, and a small amount of cobalt nitrate induces quantitative oxidation at 710° (Adadurov and Afroschtschenko, J. Appl. Chem. Russia, 1933, 6, 1029). Nickel gauze (including platinised nickel) has been tried (Adadurov and Prozorovski, *ibid.* 1935, 8, 1321).

A two-stage oxidation, first with platinum at 550° and then with iron-bismuth oxides (20% Bi<sub>2</sub>O<sub>3</sub>) or iron-cobalt oxides, is said to economise in platinum (Epschtein and Tkatchenko, *ibid.* 1933, 11, 731).

In all cases where nitric oxide and unoxidised ammonia are in contact, however, *e.g.*, in the interspace between two catalyst masses, there is a possibility of loss of fixed nitrogen by the reaction:



(Gay-Lussac, Ann. Chim. Phys. 1816, [ii], 1, 394), which is complete only at a high temperature (Baxter and Hickey, Amer. Chem. J. 1905, 33, 300).

The Bayer catalyst, ferric oxide with up to 10% (or more) of bismuth oxide, is one of the best of this type but has the disadvantage that the bismuth oxide slowly volatilises in use. A plant using it was operated at Leverkusen.

The ammonia gas is passed through a small balancing gasholder of 500 cu. ft. capacity into a large holder of 1,000 cu. m. capacity with an indicating dial. A mixture of air and ammonia containing 7–8% of ammonia is driven by separate centrifugal blowers to the converters, the air being filtered through cloth. Venturi meters control the mixture. The air passes through a cylindrical tubular heat exchanger

(B.P. 145059, 1920), 12 ft. by 12 ft., in counter-current to the hot converter gas, leaving by an 18-in. pipe, a 6-in. by-pass being also provided. The ammonia is not preheated, but passes by a 4-in. pipe to a mixing chamber between the exchanger and converter. This mixing chamber in some cases consists of an inclined cone 3 ft. long and 4 ft. in diameter, the hot air entering the base and the ammonia and cold by-passed air tangentially. The mixture passes to the converter at 300–360°.

The converters are sheet-iron cylinders lagged externally and lined with bricks, 15 ft. high and 12 ft. in external diameter. They formerly had an axial tube 3 ft. in diameter, serving to convey cold air to equalise the temperature of the catalyst, but in the newer types, which have a diameter 1<sub>3</sub> that of the older, this axial tube is omitted. The catalyst layer is deep, so that the time of contact is much longer than with platinum. There are first about 10 in. of fine granules resting on coarser granules on a perforated refractory plate. The gas passes upwards through the catalyst. The diameter of the catalyst granules varies from 5 to 10 mm. The diameter of the catalyst bed in the older type was 9 ft., the drop of pressure across it being about 10 cm. of water. The temperature of the catalyst is about 750°. The average capacity of the older units was 4,600 kg. of ammonia per day; the new converters have a capacity of 15,000 kg. per day. The capacity of the whole plant is 6,000–7,000 tons of nitrate per month, with an overall efficiency of 80–85%.

The absorption plant consists of three distinct units. These effect absorption in sodium carbonate, in water, and in sulphuric acid, respectively.

In the alkaline absorption section, each converter is connected with six towers, the first a small rectangular stone tower 12 ft. high and 3 ft. wide, acting mainly as a cooler. The second tower is cylindrical, 30 ft. high and 8 ft. diameter, of steel plates. The third tower is rectangular, of volvic stone, and 30 ft. high, whilst the remaining three towers are like the second. There are twelve rows of these towers, the gases from which pass by a common main to a 60-ft. tower 20 ft. in diameter, through which they are drawn by a fan. Saturated sodium carbonate solution is supplied to the tops of the first, second, sixth, and seventh towers, and drains to a granite tank, from which it is pumped to the top of the fourth tower, which is run slightly acid so as to cause conversion of all nitrite into nitrate (*see* p. 572*b*). From this tower the sodium nitrate solution leaves by a 4-in. main.

In the water absorption section the gas from the converters is brought by a 3 ft. main to six brick towers, 40 ft. by 12 ft., arranged in three rows of two and packed with broken quartz. From these the gas passes through a rectangular brick flue, 6 ft. by 3 ft., to twelve brick towers, 60 ft. high and 13 ft. in internal diameter, the walls being 2 ft. thick. After being drawn through these towers by a fan the gas is discharged to the free air through a 3-ft. iron pipe. Water is fed to the last tower and circulated forward by centrifugal pumps. When the acid



reaches the bottom of the fourth tower in the series of twelve it is cooled between successive towers and finally reaches a concentration of 40-50% nitric acid.

The plant for absorption in sulphuric acid consists of six steel towers, 40 ft. high and 8 ft. in diameter, the acid being cooled in coils between each pair of towers through which it is circulated. Nitric acid is recovered by distillation, although steam must be added. The results were not satisfactory on account of the difficulty of recovering nitric acid from the liquid after absorption.

I.G. Farbenind. A.-G. (B.P. 498898, 1937), specifies treating converter gas with air or oxygen to convert nitric oxide to the dioxide, concentrated nitric acid being added at the end to assist oxidation. The gas is dried by cooling and silica gel, and absorbed in 95% sulphuric acid, the nitric acid formed being distilled off at above 100° under reduced pressure. Dilute nitric acid is then added to expel oxides of nitrogen from the sulphuric acid, these being oxidised and retreated, and the residual sulphuric acid denitrated. Du Pont de Nemours (U.S.P. 2139721, 1938) feed preheated concentrated sulphuric acid and dilute nitric acid to the top of a tower at 110° and introduce sulphur trioxide near the base of the tower, when 95% nitric acid distils, and the sulphuric acid leaving the base of the tower is enriched with sulphur trioxide.

**Oxidation of Ammonia with Oxygen.** After the introduction of the multiple platinum gauze catalyst by Kaiser in 1910 (p. 563c), the next notable advance in the oxidation of ammonia was the use of oxygen instead of air. Pure oxygen and ammonia form a violently

explosive mixture until the oxygen ratio exceeds 3.5 vol. to 1 vol. of ammonia (Partington and Prince, J.C.S. 1924, 125, 2018). A successful method of obviating the explosive properties of the mixture was first protected in 1921 (Partington, U.S.P. 1378271, 1921; J. R. Partington and L. H. Parkor, "The Nitrogen Industry," Constable, 1922, p. 326), and is applied in modern technical processes of ammonia oxidation, the many other subsequent proposals, including cooling of the catalyst zone, etc., having been unsuccessful or unsuitable for technical working. The basis of the process is to replace the diluent nitrogen in atmospheric air by steam, a suitable mixture of ammonia gas, steam, and oxygen being passed through a platinum gauze catalyst in an ordinary converter. If an excess of oxygen, sufficient to form nitric acid with the nitric oxide, is used, the converter gas may be condensed to nitric acid by simple cooling, no absorption towers being necessary. A suitable proportion of steam is obtained by volatilising concentrated ammonia solution (p. 0.88) in a current of oxygen. The process may also be worked with air enriched with oxygen, a suitable amount of steam being added, but unless an oxygen-rich gas is used absorption towers will be necessary. A feature of the oxygen process is the high rate of conversion.

A comparison of the sizes and outputs of various types of platinum gauze converters is given in the following table. These results were all obtained by the writer in long runs under various conditions, with converters of cross-section 4 in. by 6 in., i.e., full-sized technical units. For comparison, the Ostwald type is given first.

Type of converter.	Catalyst.	Method of heating.	Conversion efficiency, %.	Output kg. HNO <sub>3</sub> per g. Pt per 24 hours.
Ostwald . . .	Platinum foil.	Regenerative.	90-95	1.7-2
Frank-Care . .	Single platinum gauze.	Electrical.	90-93	11
Kaiser . . .	4 superposed platinum gauzes.	Preheating of gases.	95	12
Partington . .	2 platinum gauzes slightly separated.	Electrical or preheating of gases.	95	10
Partington with oxygen.	2 platinum gauzes in contact.	Gases+steam preheated to 500-600°.	98-99	21

The loss of platinum (2.4 g. per ton of nitric acid) is said to be higher in the steam-oxygen process with a mixture of NH<sub>3</sub> 15, O<sub>2</sub> 30, and H<sub>2</sub>O 55 vol.-%, but the experiments were made at a high gauze temperature (900°) (Adadurov, Astroschenko, and Konvissor, J. Appl. Chem. Russia, 1936, 9, 1745). The normal loss has been given as 100 mg. per ton of nitric acid (Figurovski, *ibid.* 1936, 9, 37).

Under certain conditions, mixtures of air and ammonia may be explosive (Schlumberger and Pietrowsky, J. Gasbeleucht. 1914, 57, 941; White, J.C.S. 1922, 121, 1688; 1925, 127, 48; Reis, Z. physikal. Chem. 1914, 88, 513; Berl and Bausch, *ibid.* 1929, 145, 347; Jorissen and Ongkiehong, Rec. trav. chim. 1926, 45, 225; Schliephake, von Nagel, and Schoml, Z. angew. Chem. 1930, 43, 302).

Some alternatives to the steam process which

have been proposed may be mentioned. Cederberg (B.P. 244134, 1925; G.P. 531945, 558433, 1932) described a converter of chrome-nickel steel with a narrow reaction space so that a gas layer is formed sufficiently thin to prevent explosion, the platinum gauze or sheet being in this space. Yee (Ind. Eng. Chem. 1929, 21, 1024) described a water-cooled aluminium converter. Liljenroth (F.P. 610010, 610160, 1926) oxidised in stages, cooling the gas between the stages. A mixture of 9 parts of oxygen and 1 part of ammonia may also be passed through successive converters, with cooling and addition of further ammonia between each. Interaction of nitric oxide and ammonia is said not to occur (*see* p. 570b), and the final gas may contain 50% of nitric oxide (Badische Anilin- u. Soda-Fabr., B.P. 241135, 1925).

Ammonia oxidation under increased pressure

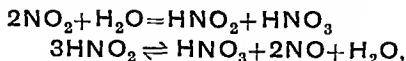


(which, theoretically, should act unfavourably on the equilibrium yield) has been worked by the Du Pont Co. at Repauno, N.J. (Taylor, Chilton, and Handforth, *Ind. Eng. Chem.* 1931, 23, 860); under 7-8 atm. an increase of 8-10% in acid concentration is obtained, with higher power cost but only half the initial cost as compared with normal pressure (*cf.* Chem. Age, 1931, 25, 568; Pauling, B.P. 334448, 1929; Synthetic Ammonia and Nitrates, Ltd., and Greathouse, B.P. 221513, 1923; Libinson, J. Chem. Ind. Moscow, 1929, 6, 8; Maliarevsky and Papkov, *ibid.* 1928, 5, 682). Fauser (*Chim. et Ind.* 1931, 25, 556; *Chem. Met. Eng.* 1930, 37, 604) states, however, that the conversion efficiency falls to 91%, and the life of the catalyst is reduced, by operating under increased pressure, so that the pressure must be applied to the oxidised gas (p. 575b).

#### ABSORPTION OF OXIDES OF NITROGEN.

The production of nitric acid by bringing gases containing oxides of nitrogen and excess of oxygen in contact with water is a process which can, and has, given rise to great technical difficulties unless the mechanism of the reactions is fully appreciated. It is completely different from the relatively simple problem of absorbing a single gas in a liquid, such as hydrogen chloride in water, or sulphur trioxide in concentrated sulphuric acid, when the only concern of the plant designer is to provide adequate absorption surface and cooling.

Nitric oxide, NO, the first product of the arc and ammonia oxidation processes, is practically insoluble in water, and the first step in the absorption process is to convert it, by spontaneous oxidation in the gas phase by excess of oxygen (which may be in the form of air), into nitrogen dioxide, NO<sub>2</sub>, by the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ . The kinetics of this termolecular reaction are fully and quantitatively known (p. 520a), so that the many speculations on it which have been made, and still appear, are pointless. With dilute gases the reaction is rather slow, and adequate gas space must be provided. The problem is, however, greatly complicated by the fact that, when the oxidised gas is brought in contact with water, nitric oxide is again formed by the reactions:



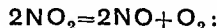
and free space for its re-oxidation is again required. The effect is that, unless the absorption system is scientifically designed, it becomes very large, expensive, and inefficient. Any attempt to bring about rapid absorption by exposure of a large surface without adequate empty oxidising space merely produces a liquid containing nitrous acid and nitrous anhydride ( $2\text{HNO}_2 \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O}$ ), which on agitation or exposure to air emits nitric oxide, only a dilute acid remaining. With increasing concentration, the nitrous acid becomes unstable, the greater part being eliminated. As the concentration of nitric acid increases, however, the nitrous acid tends to be retained and partly converted into NO<sub>2</sub> in the liquid, so that the progress of the absorption reaction becomes still

more complicated (*see* Hall, Jacques, and Leslie, *J.S.C.I.* 1922, 41, 285r; Pascal, *Mém. Poudres*, 1924, 21, 1; H. W. Webb, "Absorption of Nitrous Gases," Arnold, 1924; *J.S.C.I.* 1913, 50, 128r; *Trans. Inst. Chem. Eng.* 1929, 7, 108; Elukhen, *Khimistoi*, 1933, 5, 2203; Hennel, *Chim. et Ind.* 1933, 29, 786, 1042; Bräuer, Reitsötter, and Siebenreicher, *Angew. Chem.* 1932, 45, 727; A. Cottrell, "Manufacture of Nitric Acid and Nitrates," Gurney and Jackson, 1923).

Bodenstein and Lindner (*Z. physikal. Chem.* 1922, 100, 68) found for the velocity coefficient *k* of the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  (units g. mol. per l. and minutes):

Temp., °C.	0	30	60	90	141
$k \times 10^{-6}$	2.09	1.59	1.31	1.12	0.925
Temp., °C.	197	241	291	340	389
$k \times 10^{-6}$	0.791	0.724	0.681	0.659	0.649

and Bodenstein and Ramstetter (*see* Bodenstein and Lindner, *l.c.*) for the reaction



Temp., °C.	319	330.5	354	378.5	383
$k$	61.0	90.6	204	485	568

The equilibrium  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  was found to be given, between 9° and 115°C. by the equation:

$$\log (p_{\text{NO}_2}^2/p_{\text{N}_2\text{O}_4}) = -2,692/T + 1.75 \log T + 0.00483T - 7.144 \times 10^{-5}T^2 + 3.062$$

and the equilibrium  $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$  between 220° and 550°C. by the equation:

$$\log (p_{\text{NO}}^2 p_{\text{O}_2}/p_{\text{NO}_2}^2) = -5,749/T + 1.75 \log T - 0.00050T + 2.839$$

with *p* in atm.

The absorption towers for the dilute gases formed in the arc process are very large. At Rjukan there are 32 granite absorption towers, each 34 m. high and 7 m. in diameter, and weighing 2,400 tons.

In the Legnano works of Rossi, using the Pauling process, there is an empty oxidation tower of 70,620 cu. ft. capacity, five acid towers, each 65.6 ft. high and 16.4 ft. in diameter, and four iron alkali towers, each 72 ft. high and 11.5 ft. in diameter. The strongest acid is 23-25% HNO<sub>3</sub>, and 20% of the absorbed gas is recovered in the alkali towers. The loss is only 1%.

The enormous towers used in arc process plants were, however, inefficient on account of unscientific design.

Experiments by Prof. Pascal at Angoulême showed that three towers, 18 in. in diameter and 15 ft. high, with scientific arrangement, effect the same absorption as one of the usual granite towers 60 ft. high, weighing 260 tons and costing £4,000.

The absorption towers used for ammonia-oxidation gas at Angoulême (P. Pascal, "Traité de Chimie Minérale," Masson, 1932, Vol. III, p. 744) were 12.5 m. high and 4.15 m. in internal diameter, with an 8-m. column of packing and an internal exit pipe 35 cm. by 70 cm. reaching to 20 cm. of the top. The packing left 63% of free space and exposed a surface of 27 sq. m. per

cu. m., or 2,700 sq. m. in each tower. The acid circulation was 15 cu. m. per hour. The gas velocity was 7 cm. per sec. The concentration of oxides of nitrogen in the gas, expressed in g. of nitric acid per cu. m., and the concentration of the liquid acid in the seven absorption towers producing 10 metric tons of nitric acid as 20 tons of 50% acid, are given in the table. The initial concentration of the gas was 210-230 g. of nitric acid per cu. m.

Tower	1	2	3	4
Gas concn.	198-175	192-162	149-80	96-41
Acid concn.	53.9-48.5	49.5-41.5	41.5-32.5	32.5-20.2

Tower	5	6	7
Gas concn.	41-13	19-7	11-1
Acid concn.	20.2-10.7	10.7-5.5	5.5-0

If the temperature rose, the acid concentration in the first tower was sometimes a little smaller than that in the second. Aluminium tube coolers were interposed in the acid circuit. The loss in unabsorbed gas varied from 0.5-5%, usually 2-3%, and even 1% with good cooling. A comparison of the efficiency of the last three towers with the Norwegian granite towers is given:

	Towers 5, 6, and 7.	Norwegian towers.
Number of towers	3	4
Total useful volume	330 cu. m.	2,400 cu. m.
Total empty space	200 cu. m.	1,200 cu. m.
Time of contact (min.)	13	3
Circulation per hour		
per sq. m.	0.5-1 cu. m.	0.3 cu. m.
HNO <sub>3</sub> condensed	750 kg.	12-15 metric tons
HNO <sub>3</sub> condensed per cu. m.	2.25 kg.	5-6.25 kg.

The absorption system at Höchst is described on p. 568c.

Many papers dealing with the flow of liquid and gas through a packed tower have appeared (Scott, Trans. Inst. Chem. Eng. 1935, 13, 211; Hickson and Scott, Ind. Eng. Chem. 1935, 27, 307; Baker, Chilton, and Vernon, Trans. Amer. Inst. Chem. Eng. 1935, 31, 296; Mayo, Hunter, and Nash, J.S.C.I. 1935, 54, 375r; Tour and Lerman, Trans. Amer. Inst. Chem. Eng. 1939, 35, 709). The theory of towers for absorbing oxides of nitrogen is less advanced (Partington and Parker, J.S.C.I. 1919, 38, 75r; 1924, 43, 52r; Taylor, Chilton, and Handforth, Ind. Eng. Chem. 1931, 23, 860; Chambers and Sherwood, *ibid.* 1937, 29, 1415; Kiritschenko and Benkovski, Ukrain. Chem. J. 1936, 11, 304; H. W. Webb, "Absorption of Nitrous Gases," Arnold, 1924).

The efficiency of a tower system will depend on three factors:

1. *The rapidity and completeness of absorption.* This may be specified by the weight of soluble gas extracted per min. per cu. ft. of gross tower space, and the overall percentage absorption.

2. *The concentration of the solution produced.* This factor is of considerable importance, since the costs of handling, storing, and concentrating 30% nitric acid are much greater than those for 50% acid.

*Rapidity and completeness of absorption.*—The weight in lb. of nitrogen dioxide absorbed in 1 min. per sq. ft. of acid surface, or the *absorption coefficient*, depends on the partial pressures of nitrogen dioxide and oxygen in the

gas, the concentration of the acid used for absorption, the temperature, the turbulence of the liquid and of the gas, the amount of oxidation space allowed for the nitric oxide produced during the absorption, and the rate of renewal of liquid surface, *i.e.*, the acid flow through the tower. Values of the absorption coefficient are given by Partington and Parker (*l.c.*). The dependence on the partial pressure of nitrogen dioxide is shown by the following figures:

Gas.	% NO <sub>2</sub> in gas.	Cu. ft. gross tower space per lb. of NO <sub>2</sub> per min.
Arc	1	5,000
Deaerator	20	200

The dependence on the strength of acid used for absorption is approximately as follows:

% strength of acid.	Rate of absorption.
0	1.00
10	0.99
20	0.95
30	0.90
40	0.80
50	0.70
60	0.55
65	0.32
68	0.00

(Foerster and Koch, Z. angew. Chem. 1908, 21, 2161, 2209; Rideal, J. Ind. Eng. Chem. 1920, 12, 531; Foerster, Burchardt, and Fricke, Z. angew. Chem. 1920, 33, 113, 122, 129; Hall, Jacques, and Leslie, J.S.C.I. 1922, 41, 285r; Pascal and Decarriere, in P. Pascal, "Traité de Chimie Minérale," Masson, 1932, Vol. III, p. 750). There is evidence of a maximum speed of absorption in 10% acid.

*Elimination of Nitrous Acid.*—The primary reaction in the absorption is the formation of one molecule each of nitric and nitrous acids:  $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$ . The elimination of the nitrous acid from the liquid now follows; the final acid rarely contains more than about 0.3% of nitrous acid.

The exact mode of elimination of the nitrous acid has been differently explained.

1. *The nitric oxide theory.* According to this, the nitrous acid decomposes reversibly according to the equation:



(Sapozhnikoff, J. Russ. Phys. Chem. Soc. 1900, 32, 375; 1901, 33, 506; Lewis and Edgar, J. Amer. Chem. Soc. 1911, 33, 292; Burdick and Freed, *ibid.* 1921, 43, 518; Abel *et al.*, Z. physikal. Chem. 1928, 132, 55; 134, 279; 136, 135, 419, 430; 1930, 147, 69; 148, 337; Klemenc, Alfons, and Hayek, Z. anorg. Chem. 1930, 186, 187; Klemenc and Rupp, *ibid.* 1930, 194, 51; Bodo, *ibid.* 1931, 195, 201; Podhorsky, Archiv. Hem. Farm. 1932, 6, 187).

Lewis and Edgar found at 25°

$$K = [\text{HNO}_2]^3 / [\text{H}][\text{NO}_3] = 0.0267,$$

but later workers found that the reaction is more complex than that formulated. The value of  $K$  at 25° is approximately 0.033 but depends on the ionic strength (particularly the  $\text{HNO}_3$  concentration) in a known way.

In presence of nitric oxide gas this reaction reaches an equilibrium with nitrous and nitric acids present together in the solution. In actual tower practice, however, there is an excess of oxygen and of indifferent gas. Both factors tend to reduce the nitrous acid concentration in the solution; the first by removing the supernatant nitric oxide, with formation of nitrogen dioxide which then re-dissolves, and the second by reducing the partial pressure of the nitric oxide.

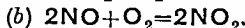
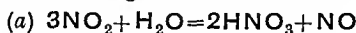
2. *The volatilisation theory.* Nitrous acid in aqueous solution above a certain strength exhibits a marked blue colour, owing to partial dissociation with the formation of  $\text{N}_2\text{O}_3$ :  $2\text{HNO}_2 \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O}$ . The  $\text{N}_2\text{O}_3$  tends to escape from the solution as  $\text{NO}$  and  $\text{NO}_2$ .

Klemenc and Pollak (*Z. physikal. Chem.* 1922, 101, 150) found that the rate of decomposition of nitrous acid solution is mainly determined by the rate at which  $\text{NO}$  escapes from the solution, and is proportional to the  $\text{HNO}_2$  concentration. The rate of decomposition is increased by passing carbon dioxide through the solution and by adding other acids.

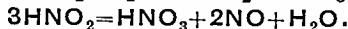
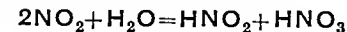
3. *The oxidation theory.* In absorption towers, where excess of oxygen is present, the reaction  $2\text{HNO}_2 + \text{O}_2 = 2\text{HNO}_3$  undoubtedly takes place in solution, and probably to a still greater extent in the Pohle lifts, where a very efficient churning together of the liquid and the air used for working the lifts occurs. The use of oxygen instead of air in working the lifts would greatly increase this oxidising action (Farbw. vorm. Meister, Lucius, und Brünig, B.P. 19032, 1911).

Under average conditions the elimination of nitrous acid proceeds at a rate sufficient to allow it to be neglected in considering the rate of solution of the oxides of nitrogen.

*Oxidising Space in Towers.*—Although some of the nitrous acid produced in the absorption towers is eliminated in solution by oxidation, the greater part reappears in the gas phase as nitric oxide, arising from the reactions:

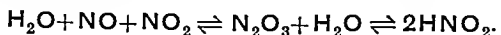


Equation (a) appears to be the sum of two separate reactions, involving the intermediate formation of nitrous acid:

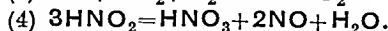
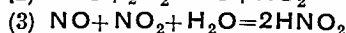
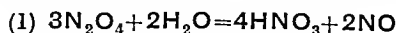


Reactions (a) and (b) constitute a cycle, in which out of three molecules of nitrogen dioxide taken, two are absorbed, and one remains for further absorption. One-third of the nitrogen dioxide therefore remains after each cycle. Thus, after four cycles, about 99% of the oxides are absorbed.

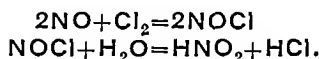
The regeneration of nitrogen dioxide by reaction (b) is not, in ordinary tower practice, carried out under ideal conditions, because the first half of the oxidation of  $\text{NO}$  to  $\text{NO}_2$  is much faster than the second (p. 520b), and the mixture of  $\text{NO}$  and  $\text{NO}_2$  so formed is rapidly absorbed by water, with the production of nitrous acid:



The cycle of reactions, under these conditions, will now be as follows:



It can be shown that, with these reactions, it is necessary to go through at least ten cycles to produce the same effect as with four cycles in which the gas presented to the liquid is fully oxidised  $\text{NO}_2$ . This will very much increase the tower space required. Patents have been framed to obviate this by removing the gas after each contact with water, and allowing it to be fully oxidised before again bringing it into contact with water or acid (*see below*). It has also been proposed to use catalysts for the oxidation of nitric oxide, e.g., a cobaltic oxide gel at 300° (Klingelhofer, U.S.P. 2115173, 1938) and vapours of iron pentacarbonyl (Ges. f. Linde's Eismaschinen A.-G., G.P. 660734, 1933). The presence of chlorine in the gas is also said to accelerate the absorption of oxides of nitrogen (H. W. Webb, "Absorption of Nitrous Gases," Arnold, 1924; J.S.C.I. 1931, 50, 128r; Trans. Inst. Chem. Eng. 1929, 7, 108) perhaps from the intermediate formation of nitrosyl chloride:



The actual conditions obtaining in towers are, however, more advantageous than would appear at first sight, for the following reasons: (i) The oxidation in the free space will proceed beyond the stage  $\text{NO} + \text{NO}_2$ , (ii) opportunity for complete oxidation will occur in the connecting pipes between the towers.

The complete oxidation of nitric oxide by atmospheric oxygen is slow in the case of dilute gases, and this reaction is the chief source of difficulty in all nitrogen fixation processes in which nitric oxide is the primary product (*see* p. 572b). It may be said that, for gas containing 2% of nitric oxide, a time of contact of not less than 2 minutes is required for adequate oxidation before subsequent absorption. In this case 90% of the  $\text{NO}$  will be oxidised to  $\text{NO}_2$  (G. W. Todd, "Physical and Chemical Data of Nitrogen Fixation," H.M. Stationery Office, 1919; Phil. Mag. 1918, [vii], 35, 281, 435; Proc. Durham Phil. Soc. 1923, 6, 291).

*Mist Formation in Towers.*—An important phenomenon which makes its appearance during the absorption of oxides of nitrogen in water is the formation of a white mist (*cf.* Chambers and Sherwood, Ind. Eng. Chem. 1937, 29, 1415), which is carried away by the inert gas passing through the towers, and appears in the exit gas. The mist consists of quite strong nitric acid in the form of droplets, which are formed as soon as the oxides of nitrogen enter the train of absorption towers, i.e., in the strong acid tower, and pass unaltered and uncondensed through the remaining weak acid towers.

In the absorption of gases from arc furnaces, the gases coming from the water towers contain a considerable quantity of acid mist, which

normally passes into the soda towers and is thoro absorbed as sodium nitrate. If soda towers are not used, this mist escapes condensation, and even with soda towers the absorption is incomplete. By means of electrical precipitation apparatus it is possible to condense the mist to 35% nitric acid, i.e., acid corresponding with that in the first tower.

In absorption-tower operation Webb (l.c.) recommends an inlet temperature of 15–40°, and with rich gas the towers should be cooled to remove the heat of oxidation of nitric oxide. Reactions in packed and unpacked towers are regarded as different. Toniolo (Chim. et Ind. 1927, 17, 546; Chem. Met. Eng. 1927, 34, 92; B.P. 267721, 1926), Taylor (Ind. Eng. Chem. 1927, 19, 1250), Kaltenbach (Chim. et Ind. 1929, 21, 701), Libinson (J. Chem. Ind. Moscow, 1932, 9, No. 10, 66), and Berl (*ibid.* No. 11, 44) also recommend cooling, and emphasise the necessity of securing as complete oxidation of nitric oxide as possible (cf. J. R. Partington and L. H. Parker, "The Nitrogen Industry," Constable, 1922, p. 326; Lüscher, U.S.P. 1901816, 1929). There is some evidence that with very dilute gases, warming the tower liquid is advantageous (Rideal, J. Ind. Eng. Chem. 1920, 12, 531).

The use of acid-resisting steel coolers and absorption towers is becoming general; in America, steel with 16–19% of chromium, less than 0.12% of carbon, less than 1% of silicon, and less than 0.4% of manganese, is used (Mitchell, Chem. Met. Eng. 1928, 35, 734; Ind. Eng. Chem. 1929, 21, 442), although McQuigg recommends 20% of chromium. The welding and heat treatment of such steels requires very special technique, otherwise rapid disintegration and corrosion of the joints ensue (Martin, Chem. Trade J. 1931, 89, 631; Leverick, J.S.C.I. 1930, 49, 472; Hatfield, *ibid.* 1929, 48, 1060; Donaldson, *ibid.* 1931, 50, 787; Becket, *ibid.* 1932, 51, 49; Matagrin, Chem. Met. Eng. 1933, 40, 480). Absorption under increased pressure is possible with use of acid-resisting steel compressors and absorption vessels. A chrome-nickel steel called V<sub>2A</sub> metal, suitable for use with nitric acid, was introduced by Krupp A.-G. at Essen (B. Waeser and E. Fyelman, "Atmospheric Nitrogen Industry," Vol. II, Churchill, 1926, pp. 674, 677). Acid pumps, including centrifugal pumps, are made of this steel.

Fausser (Chim. et Ind. 1931, 25, 556; Chem. Met. Eng. 1930, 37, 604; Chem. Age, 1932, 26, 368; Sander, Chem. Fabrik, 1932, 5, 412) oxidises a mixture containing 11% of ammonia and enriched to 22% of oxygen, without pre-heating, at atmospheric pressure, compresses the oxidised gas to 3–3.5 atm. by chromo-steel turbo-compressors, and effects absorption in horizontal acid-resisting steel cylinders, cooled externally by water, with an empty upper oxidising space, the acid passing through them in counter-current by U-pipes. The gas is admitted through a perforated horizontal tube lying near the liquid surface, and bubbles through the liquid. Twelve cylinders give an absorption efficiency of 95%. This process is used at Sluiskil, with a capacity of 120 tons of

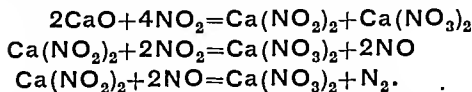
36° acid per day, and in addition to better efficiency it produces a stronger acid than towers (Berl, Z. angew. Chem. 1923, 36, 87; Fausser, Giorn. Chim. Ind. Appl. 1928, 10, 183; Van der Hoeven, Ingenieur (Holland), 1932, 47A, 293).

Many proposals have been made to absorb oxides of nitrogen without towers, or in specially designed towers. In some of these the necessity of providing adequate oxidising space is recognised. Häusser (B.P. 7419, 1914) makes provision for re-oxidation of the NO produced in the interaction between NO<sub>2</sub> and water by causing the gas to traverse a long path after each absorption. Engels and Dürre (G.P. 229096, 1908) pass gases containing not less than 50% of N<sub>2</sub>O<sub>3</sub> through a series of towers fed with water and add air in portions to each tower. Naville, Guye, and Guye (B.P. 6155, 1908, conv. 1907) allow oxides of nitrogen containing fully oxidised NO<sub>2</sub> to react with water until about two-thirds of the oxides are removed. The residual gas, containing NO, is then dried, usually by cooling, and allowed to reoxidise completely in an empty chamber out of contact with water. The fully oxidised gas is again brought in contact with water until another two-thirds is absorbed, and the process repeated. Farbw. vorm. Meister, Lucius, and Brüning (B.P. 19032, 1911) use compressed oxygen instead of air in operating acid elevators, the gas from the elevators being introduced into the towers. The Norsk Hydro. (B.P. 100099, 1915) effect absorption under pressure, when the volume is reduced proportionally to the square of the pressure (cf. Naville and Guye, F.P. 385569 and 385605, 1908, in which absorption of air furnace gas under pressure is said to give 95% nitric acid directly). Bergins (G.P. Ann. B. 53617) compresses oxides of nitrogen to 25 atm., adds steam, and expands suddenly into a chamber, when nitric acid is obtained. Moscicki (B.P. 17355, 1911; Beardsley and Park, U.S.P. 2206195, 1910) uses an absorption apparatus comprising rectangular chambers built into one block, the dividing walls being pierced with small holes. Alternate chambers are packed and empty. The width of each chamber is only 15–30 cm., and the gas flows at the rate of about 4 cm. per second horizontally through the apparatus. The absorbing chambers are flooded intermittently with liquid, which is allowed to drain off, and elevated to the top of the next chamber in opposition to the motion of the gas.

Silica gel may be used to separate nitrogen dioxide from a gas (e.g., from ammonia oxidation converters) (Krase, Chem. Met. Eng. 1926, 33, 674; Ray, J. Physical Chem. 1925, 29, 74) or air gas (Briner and Sguaitamatta, Helv. Chim. Acta, 1941, 24, 421). Krase removes water in a tower packed with water-cooled aluminium helices, when a loss of dissolved oxides as low as 1% may be realised. The gas is then passed through an oxidising tower and then through a tower with powdered silica gel falling through it. Only 34–47% of oxides are absorbed at one passage. The gas is driven out by heating the gel in a slow stream of air at 350° (McCollum and Daniels, Ind. Eng. Chem. 1923, 15, 1173). A good silica gel can be heated as high as 800°

without losing its activity. Adsorption by active charcoal has also been proposed (Verein f. Chem. u. Met. Prod., G.P. 418322, 1922).

**The Schloesing Process.**—An alternative method of absorption is proposed by A. Schloesing (F.P. 460328, 1912), in which quicklime in the form of briquettes is treated with the hot arc furnace gases for some days. Calcium nitrate and nitrite are first formed, but under the influence of the air and nitrous gases the nitrite is ultimately completely converted into nitrate. Oswald (Ann. Chim. 1914, [ix], 1, 32) found that on passing nitrogen dioxide over hot lime, a loss of 20% of combined nitrogen occurred. Oswald represents this by the equation:  $2\text{CaO} + 5\text{NO}_2 = 2\text{Ca}(\text{NO}_3)_2 + \text{N}$ , and this loss of combined nitrogen has been confirmed by Partington and Williams (J.C.S. 1924, 125, 947), who showed that the probable reactions are:

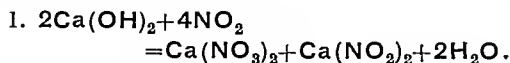


According to Schloesing, with the very dilute gases from arc furnaces, there is no loss of combined nitrogen. He lays great stress on the preparation of the lime briquettes. Quicklime obtained by burning soft chalk is slaked, the hydrate is pressed into briquettes, and the latter are dehydrated at as low a temperature as possible, about 500°. The gas must be dry and free from carbon dioxide, and is passed over the lime in lagged iron retorts at 300–400°. The use of a very porous lime is specified (Lcfort des Ylouses and L'Azote Français, U.S.P. 1959480, 1934).

Large-scale trials of the process at Notodden gave a product containing about 14% of combined nitrogen and 1–13% of free lime. This process is not worked at present.

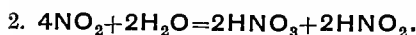
**Direct Production of Nitrates.**—Goold-Adams, Partington, and Rideal (B.P. 129699, 1917) found that if gases containing oxides of nitrogen, such as are produced in arc furnaces or by the oxidation of ammonia, are passed through an alkaline solution, containing alkali hydroxide or carbonate, lime, or a suspension of calcium carbonate (limestone, or cyanamide sludge), all the nitrite in the mixture of nitrate and nitrite first produced is ultimately converted into nitrate.

During the first part of the absorption, a mixture of equimolecular amounts of nitrate and nitrite is formed, e.g., with lime:



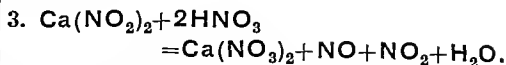
During this stage the reaction remains alkaline, and all the insoluble diluent gas (nitrogen) associated with  $4\text{NO}_2$  passes out of the apparatus.

When the reaction medium becomes neutral, the  $\text{NO}_2$  begins to dissolve as a mixture of equimolecular amounts of nitrous and nitric acids:



The nitric acid decomposes the nitrite, e.g., calcium nitrite, in solution, and a mixture of

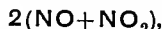
equimolecular amounts of  $\text{NO}$  and  $\text{NO}_2$  is evolved:



At the same time the nitrous acid formed in reaction (2) undergoes decomposition, with evolution of  $\text{NO} + \text{NO}_2$ :



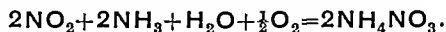
Thus, in the volume of indifferent gas which contained  $4\text{NO}_2$  on entering the apparatus we have, when it leaves the apparatus,



equivalent to the original concentration. This gas is now passed through empty towers, where the  $\text{NO}$  undergoes oxidation to  $\text{NO}_2$  in presence of the excess of oxygen in the gas. The fully oxidised gas then passes to a second set of absorbers, where reaction (1) occurs.

The final solution contains only calcium nitrate, with a little free nitrous acid, which is removed by passing air through it. This air is then passed through the absorbers containing fresh milk of lime, to recover the oxides of nitrogen. The process may be used with gas containing as little as 1% by volume of  $\text{NO}_2$ , and at the ordinary temperature or with the solutions at 30°. The milk of lime may be used of such a strength as to give a resulting solution containing 50% of calcium nitrate.

Partington, Jones, and Brownson (B.P. 134562, 136190, 1919; Sakton, J. Chem. Ind. Russ. 1936, 13, 164) found that when a mixture of air, oxides of nitrogen, and a regulated amount of moisture (e.g., suitably treated gas from the oxidation of ammonia) is passed through a chamber, and jets of ammonia gas introduced, there is an instant separation of dry, solid, ammonium nitrate, perfectly free from nitrite. This settles out as a loose powder, which on standing for a few hours shrinks to a denser powder without caking. This product is less deliquescent than ordinary ammonium nitrate, and the process gives very satisfactory yields. The mechanism of the reaction is not yet quite clear; the net result appears to be:



If oxides of nitrogen and ammonia gas are mixed without the special precautions mentioned, considerable decomposition and loss occurs. The same experimenters also found that the fume of ammonium nitrate produced when moist oxides of nitrogen and ammonia are brought together, which, unlike that formed in the above process, does not readily condense, may be brought into the solid form by passing the fume through concentrated sulphuric acid. Very little absorption of ammonium nitrate by the liquid takes place, but the dried fume at once deposits solid ammonium nitrate on issuing from the acid.

Absorption of residual traces of oxides of nitrogen in ammonia solution is proposed (Voogd, U.S.P. 2110431, 1938), but this seems likely to lead to loss as free nitrogen, from decomposition of ammonium nitrite.

Hofmann (Ber. 1926, 59 [B], 204, 2574; G.P. 469432, 1926) obtains nitrates by passing a mixture of ammonia and air over heated basic substances (alkalis, alkali carbonates, alkaline earth hydroxides except magnesia, and soda lime) to which small amounts (0.1%) of catalysts (nickel, cobalt, silver, copper, or their oxides) may be added.

Oxides of nitrogen passed at 40–50° through coarse solid ammonium bicarbonate form ammonium nitrate (F. Bartling, J. Bartling, and Meier, and Altorum Kredit A.-G., U.S.P. 1957130, 1934). Shapleigh (U.S.P. 2102136, 1937) absorbs oxides of nitrogen in ammonium nitrate solution and then adds ammonia.

**Direct Production of Concentrated Nitric Acid.**—A novel method of concen-

is a solution of nitrogen peroxide in weaker (75%) nitric acid. The upper layer may be separated and the nitrogen peroxide removed by distillation, when very concentrated nitric acid remains. The nitrogen dioxide removed is used again. These processes were verified by the writer, who found in addition that if nitrogen peroxide and oxygen are passed through water for a sufficient length of time, the same two layers are formed (J. R. Partington and L. H. Parker, "The Nitrogen Industry," Constable, 1922, p. 294; J. R. Partington, "The Alkali Industry," Baillière, 2nd ed., 1926, p. 293). This process has been developed for use in concentrating nitric acid in connection with the ammonia-oxygen-steam process for the oxidation of ammonia (p. 571c), and the method is the basis of modern processes for making concentrated nitric acid.

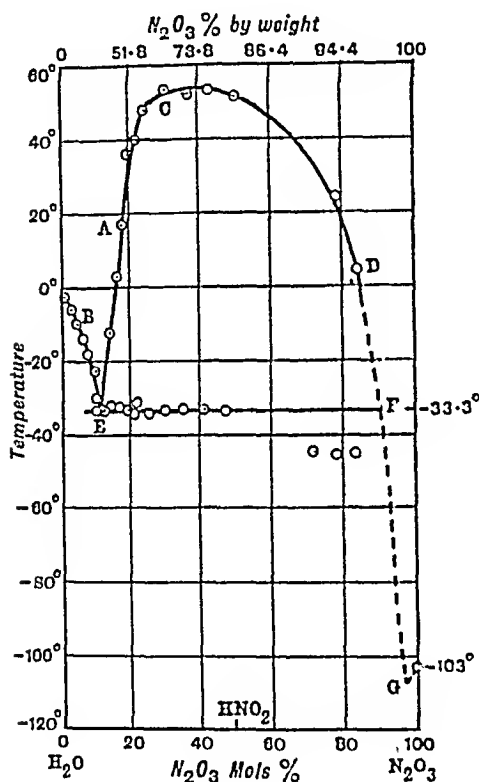
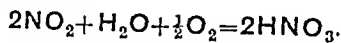


FIG. 8.

trating nitric acid is described in the patents of Farb. v. m. Moister, Lucius, and Brüning (B.P. 15948, 1911, and 4345, 1915). Acid of 60–62% is enriched with nitrogen peroxide, which readily dissolves in it, and the liquid is subjected in a finely divided condition to the action of oxygen:



The unchanged nitrogen peroxide is expelled by the current of oxygen, and the resulting concentrated acid is practically free from nitrous acid. In another process, aqueous nitric acid is agitated with excess of liquid nitrogen peroxide. Two layers are rapidly formed, each consisting of nitric acid holding nitrogen peroxide in solution. The upper layer consists of liquid nitrogen peroxide containing very concentrated nitric acid (98–99%) in solution, whilst the lower layer

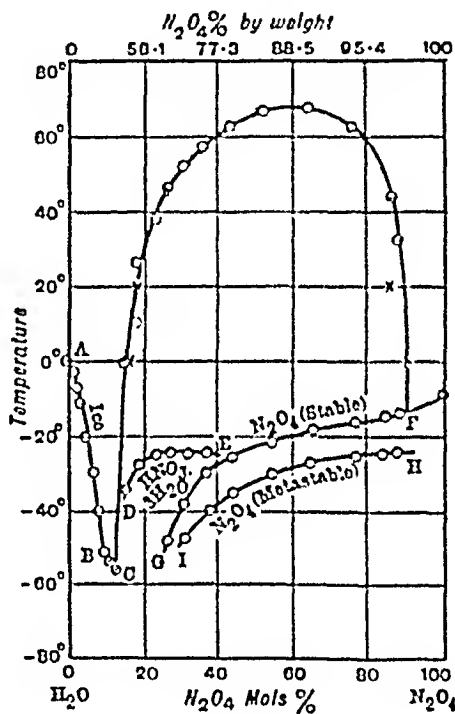


FIG. 9.

The systems involved have been (incompletely) studied by Lowry and co-workers (Lowry and Lemon, J.C.S. 1936, 1, 6; Lowry, Lloyd, and Lloyd, *ibid.*, p. 10). The equilibrium diagram for mixtures of liquid  $\text{N}_2\text{O}_3$  and water is shown in Fig. 8. Below 0° the solubility of liquid  $\text{N}_2\text{O}_3$  falls to 36% by weight at -33.3° at E, when the solubility curve intersects the freezing-point curve for homogeneous solutions of  $\text{N}_2\text{O}_3$  in water. This is a quadruple point: the aqueous liquid contains partly dissociated nitrous acid:  $2\text{HNO}_2 \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O}$ ; the heavy liquid phase (corresponding with the intersection of the horizontal at F with the curve ODF), corresponds with more than 94% of  $\text{N}_2\text{O}_3$ ; the other two phases are pure ice and a gas which is mostly NO. The compositions of the two liquid layers at other temperatures are shown by the two branches EAO and ODF of the curve, O being a critical solution temperature





aqueous components have been oxidised about half-way between  $N_2O_4$  and  $N_2O_3$  they become almost abruptly miscible with water in all proportions. The densities of the two liquid layers shewed that, whilst the non-aqueous layer was normally denser and more strongly coloured, in mixtures of  $N_2O_4$  with nitric acid, the lower layer is nitric acid with dissolved  $N_2O_4$ , whilst the upper layer is mostly liquid  $N_2O_4$  (Pascal and Garnier, *l.c.*; Bousfield, *l.c.*). Bousfield gives for the densities and compositions of saturated solutions:

HNO <sub>3</sub> in N <sub>2</sub> O <sub>4</sub> .			N <sub>2</sub> O <sub>4</sub> in HNO <sub>3</sub> .		
°	$\rho$ .	% HNO <sub>3</sub> .	°	$\rho$ .	% N <sub>2</sub> O <sub>4</sub> .
4°	1.4874	4.90	4°	1.0543	54.4
11°	1.4735	6.67	11°	1.6394	53.4
18°	1.4594	8.05	18°	1.6250	54.0

A large number of patents specify treatment of dilute nitric acid with gaseous or liquid nitrogen dioxide and oxygen or air under various conditions of temperature and pressure so as to form concentrated nitric acid:

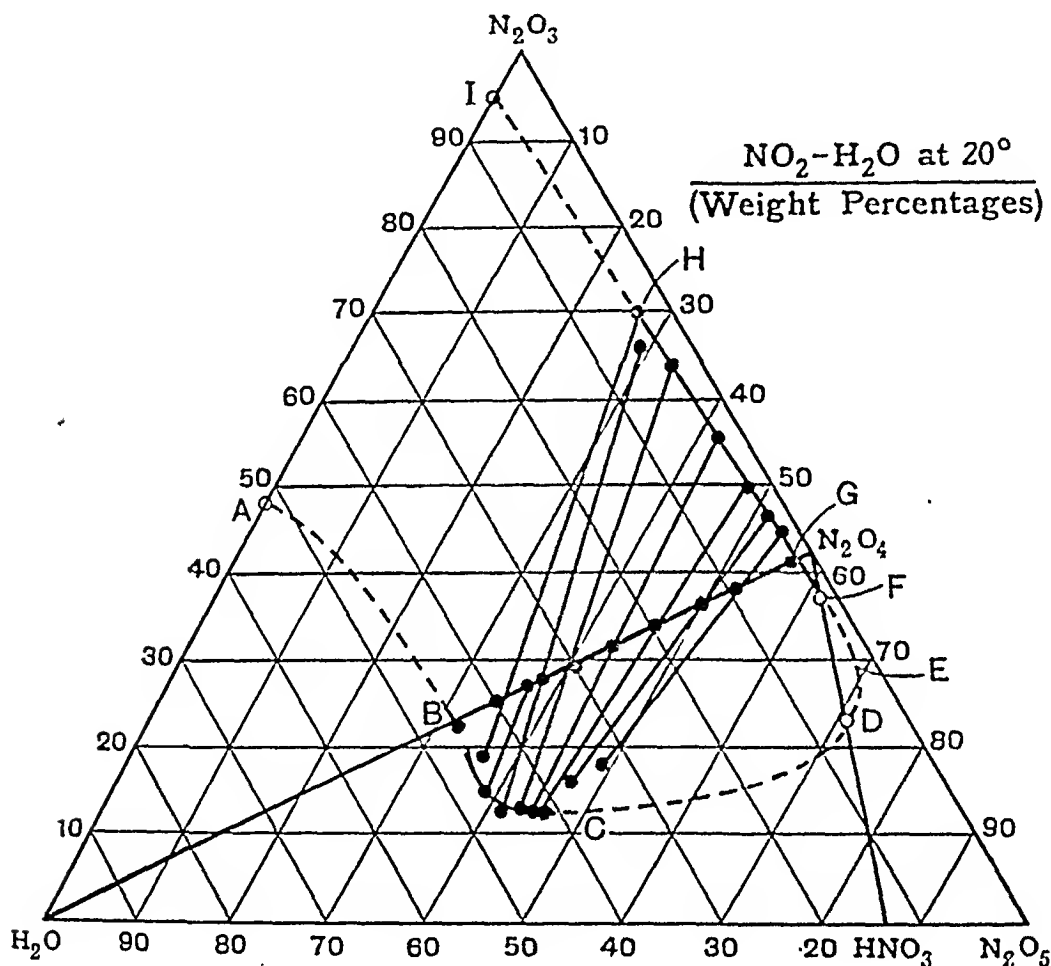
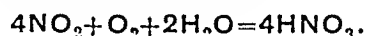


FIG. 11.

These mostly specify pre-separation of water from the converter gas by quick cooling (p. 568c) (Caro and Frank, B.P. 342068, 1929, conv. 1928, uses 50–200 atm. at 70–120° in chrome-steel tubes; I.G. Farbenind. A.-G., B.P. 320125, 321425, 321728, 325475, 1928; Collett, B.P. 362908, 1930; Melzer and von Boltensern, G.P. 440657, 1925).

Kramer and Rosenstein (U.S.P. 1948968, 1934) cool the converter gas and obtain liquid nitrogen dioxide, which forms two layers with the nitric acid, and distil. The use of oxygen and oxides of nitrogen under pressure to concentrate dilute nitric acid is proposed (Lonza Elektrizitätswerke & Chemische Fabriken A.-G., B.P. 418916, 1932). Cooling, and treatment of the dilute nitric acid with liquid nitrogen per-

oxide and oxygen at 20 atm. and 70° is specified (Caro and Frank, B.P. 405450, 1931). Caro, Frank, Wendlandt, and Fischer (U.S.P. 1989267, 1935) condense water from converter gas by cooling, cool further to condense the remaining water as nitric acid, and finally mix with air or oxygen and cool at 0° to condense liquid nitrogen peroxide. Elektrizitätswerk Lonza and E. Lüscher (Swiss P. 118714, 1925) used ozonised oxygen.

Bamag-Meguini A.-G. (B.P. 455734, 1936) pre-separate water and treat the dilute nitric acid with liquid nitrogen peroxide under pressure. The process is combined with oxidation with oxygen and steam (p. 571c), the details being as follows (Travers, *Chim. et Ind.* 1937, 38, 429; Manning, *Chem. Trade J.* 1942, 111, 499;

J.S.C.I. 1943, 62, 98). The gas mixture (ammonia, oxygen, steam) passes through a layer of water at 80° just before passing through the platinum gauze at 750° (the optimum temperature). The converter gas passes through ordinary steel tubes in a boiler and is then cooled to 200–230° by internally-cooled stainless steel tubes. It is then oxidised in a cooler of 13 vertical tubes 9 m. long cooled externally by water, in which the temperature is lowered to 25°. The rest of the water condenses and oxidation of nitric oxide to nitrogen dioxide is practically complete. At the base a 55–60% nitric acid separates, representing 18% of the nitric oxide formed. The rest of the gas is cooled by brine refrigeration to 10°, when the nitrogen peroxide liquifies. The liquid peroxide is then treated with oxygen and the 55–60% nitric acid at 50 kg. per sq. cm. pressure at 70° for four to five hours, when a mixture of nitrogen peroxide and nitric acid is formed. The gas, after liquefaction of the peroxide, is scrubbed in a tower with Raschig rings over which concentrated nitric acid at 10° circulates, the gas leaving with less than 1% of nitrogen peroxide.

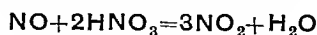
The treatment of the 55–60% nitric acid with nitrogen peroxide and oxygen occurs in an autoclave of thick-walled pure aluminium in a steel envelope, with an oxygen pressure in the annular space. It is closed by an aluminium-lined steel cover with tubes fixed in a stainless steel block. The liquids are run in at atmospheric pressure and the oxygen admitted under pressure; the reaction is rapid at 20 kg. per sq. cm. and is finished at 50 kg. per sq. cm.

The acid from the autoclave is introduced towards the middle of a column filled with Raschig rings and steam-heated at the base, the top being water-cooled. Distillation of nitrogen dioxide occurs at 90°. The 97–99% nitric acid from the base is finally bleached by a current of air.

The oxidation efficiency of the Bamag process is 96.5%, the absorption efficiency 98%, and the overall efficiency 94.5%.

Du Pont de Nemours (B.P. 456446, 1934; Davies and I.C.I., B.P. 456518, 1936) pre-remove water and absorb the nitrogen dioxide in 90% nitric acid at 0–10° and 3–5 atm. pressure. The liquid is then oxidised by air at 60–120° and 50–200 atm. pressure, dilute nitric acid being finally added to form 96% nitric acid. De Jahn and Bower (U.S.P. 2027578, 1936) specify absorption of oxides of nitrogen under pressure. Pronin (Khimistroi, 1935, 7, 395) specifies a temperature of 70° for treatment of dilute nitric acid, liquid nitrogen peroxide, and oxygen in an aluminium autoclave to make the 97–98% acid.

Variations of the process are specified in which gaseous nitrogen dioxide from de-watered and oxidised converter gas is passed in a tower at 80–90° and the 80% nitric acid formed treated in a second tower at 0° with gas from the first tower (Du Pont de Nemours, U.S.P. 2088057, 1937), or converter gas containing nitric oxide is passed in counter-current to cold nitric acid in one tower, when the reaction

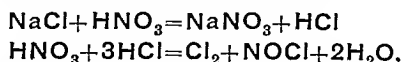


occurs, and the gas containing nitrogen dioxide

is then passed counter-current to the acid from the first tower (Chemical Construction Corp., U.S.P. 2098953, 1937; Rudbach, B.P. 481629, 1936).

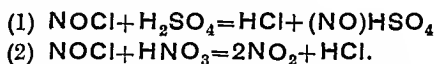
**Production of Nitrates and Chlorine.**—Much patent activity has recently centred around the treatment of common salt with nitric acid so as to form, ultimately, sodium nitrate and chlorine; the demand for the latter may exceed that for the caustic soda obtained along with it in the electrolytic process.

The reaction between sodium chloride and nitric acid is:

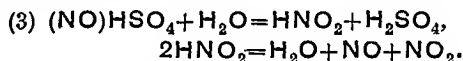


and the treatment of the gas, containing nitrosyl chloride, NOCl, and chlorine, thus brings in the same problems as were encountered in the old Dunlop process for the manufacture of chlorine (B.P. 11624, 1847; Taylor, B.P. 13025, 1884; Lunge and Pelet, Z. angew. Chem. 1895, 8, 3; Reusch, Chem.-Ztg. 1914, 38, 485; G. Lunge, "Sulphuric Acid and Alkali," Gurney and Jackson, 1911, Vol. III, p. 506).

Two reactions of nitrosyl chloride could be important in such processes:



The nitrososulphuric acid is decomposed by water:



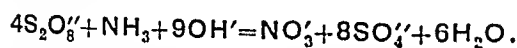
Interaction of sodium chloride and nitric acid to form sodium nitrate and nitrosyl chloride is specified by Beekhuis jun. (U.S.P. 2208112, 1940; 2215450, 1940; 2215451, 1940). Lundstrom and Whittaker (U.S.P. 2038083, 1936) oxidise nitrosyl chloride to nitrogen dioxide and chlorine by mixing with oxygen, drying, and heating to 190–300°. The Solvay Process Co., assignee of the Atmospheric Nitrogen Corp. (Canad. P. 363800, 1937; 3666786, 1937) treat sodium chloride with nitric acid, condense the nitrosyl chloride, and oxidise it to nitrogen dioxide and chlorine, which are recovered separately. Imperial Chemical Industries (B.P. 517174, 1937) treat sodium chloride solution with nitric acid, with gradual heating. The sodium nitrate is separated by cooling and subsequent neutralisation of the mother-liquor with sodium carbonate and evaporation. The gaseous product, containing chlorine, nitrosyl chloride, and nitrogen dioxide, which is evolved, is cooled and caused to react with solid sodium chloride, forming sodium nitrate and an equimolecular mixture of nitrosyl chloride and chlorine, which are separated by liquefaction and fractional distillation. The nitrosyl chloride is caused to react with sodium nitrate, forming sodium chloride and nitrogen dioxide, which is converted into nitric acid. The Solvay Process Co. (U.S.P. 2124536, 1938; 2130519, 1938; 2138016, 1938; 2228273, 1941; 2247470, 1941) convert nitrosyl chloride into nitrogen dioxide and chlorine by reaction with nitric acid. The Allied Chemical and Dye Corporation of America is

said to have made 10,000 tons of chlorine per annum by some such process (do Jahn, *Chem. Met. Eng.* 1935, 42, 537). Pauling (B.P. 452628, 1935) distils hydrochloric acid by steam heating under reduced pressure from sodium chloride and 40% nitric acid and so avoids the formation of sodium chlorate and nitrosyl chloride. Hot gas at 300–500° can be used instead of steam for heating (I.G. Farbenind. A.-G., B.P. 463811, 1935).

In some specifications (Whittaker and Lundström, U.S.P. 1920333, 1933; Kali-Forschungs-Anstalt G.m.b.H., B.P. 398187, 1933; 406553, 1934) oxides of nitrogen (e.g., from ammonia oxidation) are passed over a chloride, e.g., potassium chloride. Reed and Clark (*Ind. Eng. Chem.* 1937, 29, 333) passed a 5.2–11.0% nitrogen dioxide–air mixture in counter-current over moist solid potassium chloride; half the nitrogen oxides are converted into potassium nitrate and the other half into nitrosyl chloride, reaction being complete with a mixture containing 8% of nitrogen dioxide. With dry potassium chloride the reaction is incomplete (Whittaker, Lundström, and Merz, *ibid.* 1931, 23, 1410).

#### Oxidation of Ammonia in Solution.—

Apart from bacterial oxidation (p. 544a), many other methods of oxidation of ammonia or ammonium salts to nitrites and nitrates in solution have been investigated. The reactions with common oxidising agents mostly give nitrogen:  $2\text{NH}_3 + 3\text{O} = \text{N}_2 + 3\text{H}_2\text{O}$ . Ammonia is rather stable to many oxidising agents, although it is rapidly decomposed by chlorine, hypochlorites, bromine, and hypobromites (p. 504d). Permanganate acts very slowly in dilute solutions at room temperature, more rapidly at 60°, the reaction being influenced by the ammonia concentration. Increase in ammonia concentration increases the amounts of nitrogen and nitrite formed, and decreases the formation of nitrate. Addition of ammonium salts markedly increases the formation of nitrate and reduces that of nitrogen and nitrite; alkali increases the yield of nitrogen at the expense of nitrite (Herschkowitsch, *Z. physikal. Chem.* 1909, 65, 93). With persulphates the oxidation product is mostly nitrogen (Kempf, *Ber.* 1905, 38, 3972; Levi and Migliorini, *Gazzetta*, 1908, 38, ii, 10): with excess of persulphate at room temperature, however, over 88% of the ammonia is oxidised to nitrate:



In acid solution in presence of silver sulphate, persulphates oxidise ammonium salts nearly quantitatively to nitric acid.

Ammonia undergoes autoxidation on exposure to air in presence of copper, for example, appreciable amounts of nitrate and nitrite being formed (Berthelot, *Compt. rend.* 1863, 56, 1170; Loew, *J. pr. Chem.* 1878, [ii], 18, 298; Traube, "Ges. Abhandlungen," 1899, 393; Smith, *Proc. C.S.* 1906, 22, 39). Electrolytic anodic oxidation in presence of copper salts as catalysts converts ammonia first into nitrite and then into nitrate; with alkali present, the oxidation to nitrite proceeds continuously and is independent of the nitrite content of the solution, whilst with

decreasing alkali, the oxidation to nitrate becomes more prominent and in solutions containing no free alkali it is the sole reaction, all the nitrite formed being oxidised (Traube and Biltz, *Ber.* 1904, 37, 3130; 1906, 39, 166; Müller and Spitzor, *ibid.* 1905, 38, 778; Frenzel, *Z. anorg. Chem.* 1902, 32, 319; Fichter and Kappeler, *Z. Elektrochem.* 1909, 15, 937; 1910, 16, 610; *Chem.-Ztg.* 1912, 36, 606).

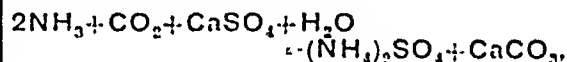
Ammonium nitrate is formed by electrolytic oxidation of ammonia solution containing 16% of ammonium bicarbonate and 0.9% of cupric hydroxide in a cell with porcelain diaphragms and iron electrodes. With a current density of 750 amp. per sq. m. and with a constant feed of ammonia to the cell a 30% solution of ammonium nitrate was obtained (Kobozov, Monblanova, and Schneerson, *J. Chem. Ind. Russ.* 1937, 14, 1307).

#### PRODUCTS OF NITROGEN FIXATION.

A brief survey of the products of nitrogen fixation will be given (*cf.* Bongueret, *J. Agr. prat.* 1932, 96, 224; Mittasch, *Z. angew. Chem.* 1928, 41, 902; Guyer and Schütze, *Angew. Chem.* 1933, 46, 763).

##### 1. Ammonium Salts include:

(a) *Ammonium Sulphate*, which is largely made from synthetic ammonia by the so-called "gypsum process" (Badische Co., G.P. 300724, 1916; *cf.* G.P. 299752, 1916; Wride, *Chem. Age*, 1920, 2, 32; Cottrell, *ibid.* 1924, 11, 282, 310, 650; Anon., *ibid.* 569, 650; Parrish, *ibid.* 1930, 24, 23; *Chem. Trade J.* 1931, 89, 504), depending on the interaction of ammonia solution, finely powdered anhydrite, and carbon dioxide, calcium carbonate being precipitated:



and removed by rotary filters. The calcium carbonate may be dried and mixed with an equal weight of ammonium nitrate to form a fertiliser called "Nitro-chalk" containing 15.6% of N (*J.S.C.I.* 1930, 49, 391n). A similar Norwegian product ("Nitrammonia-chalk") contains 20.5% of N (*Chem. Trade J.* 1931, 89, 250). The carbon-dioxide pressure has no influence on the reaction (Doroff and Troitskaja, *Ukrain. Chem. J.* 1931, 6, 123). In a modification of the process proposed by Band (*Compt. rend.* 1927, 185, 1138; Waeser, *Brennstoff-Chem.* 1930, 11, 396; Teletov *et al.*, *Ukrain. Chem. J.* 1932, 7, 141) a mixture of gypsum, clay, and ammonia solution is heated at 48–70° in a current of carbon dioxide and the residue burnt for cement. By supplying continuously calcium sulphate and ammonium carbonate to a saturated solution of ammonium sulphate, a precipitate of calcium carbonate which filters easily is formed (Knustdinger-Patent-Verwertungs A.-G., B.P. 355098, 1930).

Claudio (*Compt. rend.* 1911, 213, 105) modified the gypsum process by adding ammonia to the solution to precipitate 75% of the ammonium sulphate. The calcium carbonate formed is not washed but dried, and the product, containing ammonium sulphate, used as a fertiliser.

(b) *Ammonium Chloride* is made in tough fibrous crystals by the direct union of gaseous ammonia and hydrogen chloride containing a controlled amount of hydrogen, under such conditions that the reaction temperature is considerable (Moore, Polack, and Castner Kellner Co., B.P. 273093, 1926).

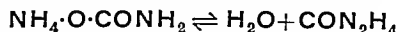
Ammonium chloride is also recovered by crystallising the mother-liquor from the bicarbonate filters in the ammonia-soda process using synthetic ammonia, and can be used as a fertiliser (Z. angew. Chem. 1918, 31, 653; Chem. Ind. 1919, 42, 438).

(c) *Ammonium Phosphates* and mixtures, e.g., "*Ammophos*" (American), ammonium sulphate and  $(\text{NH}_4)_2\text{HPO}_4$ ; "*Leunaphos*" (German), ammonium sulphate and  $(\text{NH}_4)_2\text{HPO}_4$  (non-caking granules: Klugh, Chem. Age, 1932, 26, 274); the Liljenroth process (see p. 550b) may lead to expansion of the use of these products.

(d) *Ammonium Nitrate*, which has a high nitrogen content but is explosive and deliquescent (Symes, Chem. Met. Eng. 1911, 26, 1069; Krase, Yee, and Braham, *ibid.* 1925, 32, 241; Kershaw, Ind. Eng. Chem. 1926, 18, 4; J.S.C.I. 1930, 49, 804; Hercules Powder Co., U.S.P. 1613334, 1927; non-deliquescent ammonium nitrate, Callery, B.P. 383873, 1932; A. M. Smith, Chem. and Eng. News, 1943, 21, 2100), has been used mixed with the sulphate, e.g., Leuna saltpetre,  $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$  (Bowen, J. Physical Chem. 1926, 30, 721; Osaka and Inouye, Jap. J. Chem. 1925, 2, 87), an explosion of stocks of which at Oppau in 1921 killed 559 persons and destroyed 1,036 buildings (Trans. Faraday Soc. 1924, 20, 46). In the Kuhlmann works at La Madeleine, equivalent quantities of ammonia and nitric acid are introduced into a vat containing ammonium nitrate solution, which is drawn off as produced through a cooler. The liquor is neutralised with ammonia if necessary, and evaporated in steam-jacketed aluminium tubes, then run to crystallisers which at the same time are kneading troughs, the salt solidifying to a fine white powder, practically anhydrous (Chem. Trade J. 1931, 89, 471). Fauser (Industr. Chimica, 1932, 7, 1343) sprays nitric acid into ammonia gas. The Fauser process of neutralising under pressure is rapidly extending (Tamisé, Chim. et Ind. 1933, 29, spec. no. 906; Pastonesi, Chim. e L'Ind. 1936, 16, 511). The absorption is carried out under hydrostatic pressure to prevent boiling in the reaction zone (Falk, Chem. Met. Eng. 1941, 48, No. 2, 121).

Mixtures of ammonium nitrate and calcium carbonate are sold under various trade names, such as "*Nitrochalk*," and "*Kalkammonsalpeter*."

(e) *Ammonium Carbamate* for synthetic urea obtained by heating it under pressure:



(Fichter and Becker, Ber. 1911, 44, 3473; Lewis and Burrows, J. Amer. Chem. Soc. 1912, 34, 1515; Krase and Gaddy, *ibid.* 1930, 52, 3088; Ind. Eng. Chem. 1922, 14, 611; Klemenc, Z. Elektrochem. 1930, 36, 799; Jänecke and Rahlfs, *ibid.*, p. 645; numerous patents).

2. *Nitrates*, especially calcium nitrate (direct production from oxides of nitrogen: Goad-Adams, Partington, and Rideal, B.P. 129699, 1917; Schloesing, F.P. 609264, 1925; Briner and Lugrin, Helv. Chim. Acta, 1930, 13, 76; Atm. Nitrogen Corp., F.P. 747384, 1932; Kali Forschungs-Anstalt, G.P. 566831, 1929—from potassium chloride; L'Azote Française, G.P. 558150, 1931). Calcium nitrate is made at the Kuhlmann works at La Madeleine by evaporating the solution until it will solidify and give a product containing 13% of N, cooling somewhat and feeding to the trough of a rotary drum cooler, from which the solidified nitrate is removed and ground (Chem. Trade J. 1931, 89, 471; cf. Norsk-Hydro, Norw. P. 51527, 51683, 1932). "*Nitrophoska*" is a German mixture of potassium nitrate and ammonium phosphate, practically a complete fertiliser. For analysis of nitrates, etc., see E. Berl and G. Lunge, "Chem.-tech. Untersuchungsmethoden," Berlin, 1932, II, i, 571, 581, 610; Z. angew. Chem. 1932, 45, 22.

3. *Cyanamide* may be mixed with basic slag, potassium salts, superphosphate of lime, etc.

#### STATISTICS.

The world production of fixed nitrogen, in thousands of metric tons, by various processes, is given below (from "British Sulphate of Ammonia Federation, Ltd., Annual Report," 1937-38). The "other forms of nitrogen" include nitrogen products used for industrial purposes (except Chile nitrate) and ammonia in mixed fertilisers. Fertilisers are included under the final form as sold, so that cyanamide, for example, if converted into ammonium sulphate is included under "Synthetic  $(\text{NH}_4)_2\text{SO}_4$ " and if converted into "*Ammophos*" under "Other forms of N." By-product ammonium sulphate and Chile nitrate are included for comparison. The year ending June 30 is used.

	1928-29	1929-30	1930-31	1931-32	1932-33	1933-34	1934-35	1935-36	1936-37	1937-38
Synthetic $(\text{NH}_4)_2\text{SO}_4$	485	442	349	522	560	535	533	630	688	765
By-product $(\text{NH}_4)_2\text{SO}_4$	376	425	360	302	253	307	321	376	429	411
Cyanamide	192	264	201	134	168	195	232	269	291	305
$\text{Ca}(\text{NO}_3)_2$	136	131	110	79	118	107	153	156	179	195
Other forms of N:										
Synthetic	383	427	393	348	462	516	607	724	851	931
By-product	51	51	31	30	40	48	45	46	53	49
Chile nitrate	490	464	250	170	71	84	179	192	206	224
Total	2,113	2,204	1,694	1,585	1,677	1,792	2,070	2,393	2,697	2,880

**NITROGEN FIXATION, BIOLOGICAL.** A very considerable literature has now accumulated on the subject of biological nitrogen fixation and much of this has been admirably summarised by Perry Wilson, "Biochemistry of Symbiotic Nitrogen Fixation," 1940, University of Wisconsin Press, Madison, U.S.A. The reader is referred to this book for details and references which it will not be possible to mention in the following brief article.

Two major means of biological nitrogen-fixation are recognised to-day, the first by the root-nodule bacteria living in symbiosis with certain leguminous plants, the second by special classes of bacteria living in the soil independently of the plant.

*Historical.*—The importance of leguminous crops for soil-building purposes was well known to Greek and Roman farmers. Columella, in a book written in the first century A.D., gave detailed instructions for the cultivation of such legumes as alfalfa, vetches, peas, beans, lupins, and lentils and advocated principles of green manuring well recognised and extensively adopted to-day. He advised, for example, the ploughing in of lupins as a manure when the plants were young and that residues should be ploughed in when fodder was taken. Procedures such as these were, of course, quite empirical and no reasons of any scientific merit were advanced to explain their importance.

During the seventeenth century the seeding of leguminous crops, especially clover and trefoil, as a means of improving the soil, was encouraged in English agriculture. At the same time mixed cropping (e.g., clover and rye grass) was advocated for improvement of soil tilth and production of a good herbage.

Boussingault in 1837 carried out the first quantitative field and laboratory experiments, making it clear that fixation of atmospheric nitrogen took place during the development of legumes such as clover, peas, and lucerne, whereas no such fixation occurred during the growth of such crops as wheat or oats.

Liebig (1843, 1852) was opposed to the view that free nitrogen of the atmosphere was assimilated by the plant. He considered that the beneficial effects of the legumes were due to their large leaf surfaces and consequently greater areas for absorption of atmospheric ammonia. He criticised Boussingault's results on the basis of faulty estimations of nitrogen in the manures.

Ville (1855), however, showed that atmospheric ammonia was insufficient to account for the observed increases of fixed nitrogen in the development of legumes, and made experiments in which plants were grown on ignited sands in an atmosphere which had been washed free of ammonia. He showed that all species of plants—cereals as well as legumes—made excellent growths with large increases of fixed nitrogen. He did not press his claim, however, that non-leguminous plants could derive their nitrogen from the air.

The subject remained in a confused state until after the work of Lawes, Gilbert, and Pugh at the Rothamsted Experimental Station. In 1851 they began experiments to explain the

results of field trials which had extended over 16 years. These had shown that plots cropped to non-legumes without addition of manures declined to a low yield, whereas plots cropped to legumes maintained a high yield even without manurial treatments. Moreover, if a non-legume followed a legume in a rotation, the yield was as high as if the field had been previously in fallow for a year, in spite of the large quantity of nitrogen removed in the preceding leguminous crop. Liebig's explanation of absorption of atmospheric ammonia was shown to be untenable, partly because of the inadequate quantities involved, and partly because of the difference in behaviour between legumes and non-legumes. The logical deduction appeared to be that legume development in the field was accompanied by fixation of atmospheric nitrogen. Careful pot experiments, however, by Lawes *et al.* (1861) gave rise to the conclusion that no fixation of molecular nitrogen took place during the development either of legumes or cereals and as a result it was accepted for the following 25 years that plants could not fix atmospheric nitrogen. The clear-cut results of the Rothamsted *field* experiments still remained unexplained.

The classical work of Hellriegel and Willfarth in 1866 eventually cleared up the situation. They showed that certain bacteria in the soil infected the legumes, forming nodules which enabled the plants to use atmospheric nitrogen; these bacteria had no infective power on cereals. Legumes grown in sterile sand in the presence of combined nitrogen (nitrate) grew well, with no fixation of atmospheric nitrogen. Those grown in a sterile sand and in the presence of an extract of rich garden soil developed nodules and fixed atmospheric nitrogen. Cereals were dependent entirely on a source of combined nitrogen for their development.

Thus it became apparent that biological nitrogen fixation as observed in the plant is partly, if not wholly, a bacteriological phenomenon. The organisms responsible were known as root-nodule bacteria or *Rhizobium*. They were first isolated in pure culture by Beijerinck.

#### Nitrogen Fixation by *Rhizobium*.

Little is known as yet of the mechanism of nitrogen fixation by the root nodule bacteria in association with the plant. Whereas early experiments (e.g., Golding, J. Agric. Sci. 1905, 1, 59) indicated that the *Rhizobia* are able to fix atmospheric nitrogen in the absence of the plant, this view is now discredited (Allison, J. Agric. Res. 1920, 39, 893; Hopkins, Soil Sci. 1920, 28, 433; Löhnis, *ibid.* 1930, 29, 37). Wilson, Hopkins, and Fred (Arch. Mikrobiol. 1932, 3, 322) repeated Golding's work and could find no evidence that *Rhizobia* fix nitrogen independently of the plant. Verner and Kovalov (Compt. rend. Acad. Sci. U.R.S.S. 1936, 4, 325) concluded that the addition of an extract prepared from yeast, pea, or carrot to a nitrogen-free medium will enable *Rhizobia* to fix atmospheric nitrogen. Wilson (Ergebn. Enzymforsch. 1939, 8, 13), however, failed to confirm this result. A variety of substances, having stimulating effects upon cell development, also

fail to induce nitrogen fixation by *Rhizobia* when cultured in absence of the plant. Interpretation of results were complicated by the fact that *Rhizobia* develop very readily in a medium containing most minute quantities of combined nitrogen, present possibly as an impurity. Much of the growth consists of a gum formed by the organism from the carbohydrate constituents of the medium and there is no evidence that the growth contains more nitrogen than was originally present, even as impurity, in the medium. Winogradsky (Ann. Inst. Pasteur, 1936, 56, 222) has made careful experiments in which *Rhizobia* were grown on silica gel plates containing glucose and mineral salts. Increases in nitrogen from  $3\mu\text{g.}$  to  $53\mu\text{g.}$  per plate were noted. On the other hand, the addition of combined nitrogen to plates led sometimes to losses of nitrogen, sometimes to gains.

The evidence indicates that if *Rhizobia* can fix atmospheric nitrogen on laboratory media and in absence of the plant, the experimental conditions for clearly demonstrating this have not yet been secured.

Since there is equally little evidence that the host plant, in absence of *Rhizobia*, can fix atmospheric nitrogen (see Wilson, *l.c.*), it follows that some chemical interchange between the bacteria and the plant must take place *in vivo* which is largely responsible for the nitrogen fixation. Either this is true, or there is some further biological factor (perhaps another soil organism) hitherto neglected which causes the association of *Rhizobia* and plant to take up atmospheric nitrogen. The latter alternative, however, even if true, makes for no simplification of the chemical problem which aims at establishing the mechanism whereby molecular nitrogen is brought into combination in the living cell. Wilson, Hopkins, and Fred (Soil Sci. 1931, 32, 251) have made it clear that red clover plants can fix nitrogen in the absence of all micro-organisms except *Rh. trifolii*. Virtanen, Hausen, and Laine (J. Agric. Sci. 1937, 27, 332) have also shown that a pea plant can take up atmospheric nitrogen in the absence of all organisms except *Rh. leguminosarum*.

The excised nodules do not, themselves, fix atmospheric nitrogen (Beijerinck, Verzamelde Geschriften, 1922, 5, 264; Wilson, Hopkins, and Fred, Arch. Mikrobiol. 1932, 3, 322; Galestin, Chem. Weekblad., 1933, 30, 207; Allison, Ludwig, Hoover, and Minor, Nature, 1939, 144, 711). Virtanen and Laine have claimed that the addition of neutralised oxalacetic acid to excised Torsdag pea-nodules causes fixation of nitrogen, but this claim could not be substantiated by Wilson (*l.c.*).

The chemical nature of the association between nodule bacteria and the host plant, which results in nitrogen fixation, is as yet unknown. Much, however, is now known of the biological aspects of the association between the *Rhizobia* and host plant. A lengthy discussion of these is not relevant to the scope of this article. Details are to be found in Perry Wilson's book (*op. cit.*) and may be summarised as follows:

1. When the seed of a legume germinates in a soil containing *Rhizobia* the latter are attracted to the region of the developing root hairs. The

result of the presence of the *Rhizobia* in the near neighbourhood of the root hairs is to produce a deformation or "curling" of the hairs. Such curling is induced by a specific chemical substance, since bacterial extracts, in absence of the *Rhizobia*, are as effective as the bacteria themselves. This response is biologically non-specific. Extracts of a variety of bacteria, other than the *Rhizobia*, will induce this curling. At the site of the deformation of the root hair, *Rhizobia* invade the root tissue and grow inside the root hair in a thread towards the cells of the root. The bacteria in this migration are embedded in a gum and an infection thread is formed while a sheath is laid down by the host cells around the embedded bacteria. The presence of the latter induces polyploidy in the neighbouring plant cells. Cell division is stimulated and the newly formed tissues are invaded by more bacteria (see E. B. Fred, I. L. Baldwin, and E. McCoy, "Root Nodule Bacteria and Leguminous Plants," Univ. of Wisconsin, Madison, 1932). A nodule is formed in this manner. It consists of a cap of uninfected cortical tissue cells, behind which is a region of uninfected rapidly growing cells and behind this are the larger infected cells filled with *Rhizobia*. Thimann considers that the *Rhizobia* produce in the root hair a specific substance, probably indole-3-acetic acid, which is responsible for the local stimulation of the host cells (Thimann, Proc. Nat. Acad. Sci. 1936, 22, 511; Trans. Third Comm. Intern. Soil Sci. 1939, A, 24). Both the bacteria and the host cells fail to proliferate as the nodule ages and finally the tissue becomes necrotic. The nodule becomes soft, its interior is digested and it finally sloughs off, the *Rhizobia* returning to the soil.

2. Strains of *Rhizobia* differ widely in their abilities to cause nitrogen fixation in the plant, though nodules may be readily produced by all. Nodules from inefficient strains (*i.e.* inefficient in benefiting the host plant by nitrogen fixation) are small, round, and white, and scattered over the entire root system. Nodules from efficient strains are fairly large, relatively few in number, pink in colour, elongated and situated near the main roots. The cause of the differences in efficiency in nitrogen fixation between the various strains is not yet known. Thornton (*ibid.* 1939, A, 20) considers the difference to be purely quantitative, an efficient strain being one the nodule of which persists intact for a much longer period than that of an inefficient one. Both strains may be equally effective in fixing nitrogen during the period of healthy integrity of their nodules.

3. A host-plant specificity exists, whereby a strain of *Rhizobia* is more effective in causing nitrogen fixation in one host plant than in another.

4. The presence of combined nitrogen (*e.g.*, nitrates or ammonium salts) in the soil in which the host plant is growing apparently makes the plant resistant to attack by the *Rhizobia*. It had long been known that nitrates impede the development of nodules on legumes (Rautenberg and Kühn, 1864). Fewer root hairs are deformed and fewer nodules are formed (see



Thornton and Nicol, J. Agric. Sci. 1936, 26, 173; Thornton, Proc. Roy. Soc. 1936, B, 119, 474). The net result is that when excess combined nitrogen is available to a plant little or no fixation of atmospheric nitrogen takes place. The presence of carbohydrate diminishes the inhibitory effect of combined nitrogen. It is evident that the ratio of carbohydrate to combined nitrogen affects the rates of nodule development and nitrogen fixation. The mechanism whereby the carbohydrate-nitrogen relationship in the legume affects the fixation of nitrogen is still unknown.

It has been shown from experiments with artificial media that the proliferation of *Rhizobia* depends on the presence of vitamin-B<sub>1</sub> and of biotin.

### Non-symbiotic Nitrogen Fixation.

Winogradsky (Compt. rend. 1893, 116, 1385; 1894, 118, 353) found that the inoculation of soil into a nitrogen-free medium containing glucose gives rise to a fixation of atmospheric nitrogen. He isolated the responsible organism (*Clostridium pastorianum*) which was found to be an anaerobe. This organism develops anaerobically in a glucose medium assimilating molecular nitrogen, the amount of nitrogen fixed being proportional to the glucose broken down. The fixation of nitrogen, however, is inhibited by the presence of ammonium salts. This inhibition is counteracted by an increase in the glucose concentration. Thus a carbohydrate combined-nitrogen balance determines the rate of fixation of nitrogen, as was shown 40 years later to be the case also for *Rhizobia* growing symbiotically with the host plant. Winogradsky suggested that the fixation is due to a combination of nitrogen with the hydrogen produced during the glucose fermentation. *Clostridium pastorianum* loses its power of nitrogen fixation during prolonged cultivation on laboratory media, but the power is restored by culture of the organism once again in soil (Bredemann, Zentr. Bakt. 1909, II, 23, 385).

Bejerinck (ibid. 1901, II, 7, 561) isolated from soil and mud two organisms, one a motile form, which induces nitrogen fixation in a nitrogen-free medium. These organisms are aerobes and are known as *Azotobacter chroococcum* (the more common form) and as *Azotobacter agilis* (the motile variety). These organisms grow well under aerobic conditions on nitrogen-free agar media containing glucose, mannitol or a propionate. Unlike *Clostridium*, *Azotobacter* do not lose their power of fixing nitrogen on prolonged culture on synthetic laboratory media.

There is evidence that nitrogen fixation takes place in organisms of the *Amylobacter* type, possibly related to *Clostridium* (Bredemann, l.c.), and to a small extent in certain moulds (Stahl, Jahrb. wiss. Bot. 1911, 49, 36) and in a few yeasts (Lipman, J. Biol. Chem. 1911, 10, 169). The blue-green alga *Nostoc* (Allison and Hoover, Trans. Third Int. Cong. Soil. Sci. 1935, 1, 145; Allison, Hoover, and Morris, Bot. Gaz. 1937, 98, 433) has a high nitrogen-fixing power, which is dependent to some extent on the carbohydrate supply.

*Azotobacter* and *Clostridium* are apparently

the most widely distributed non-symbiotic nitrogen fixers in soil and they are found also in salt and fresh water, often in association with algae. *Azotobacter* is not prevalent in acid soils such as peat. Its growth in artificial laboratory media may be greatly stimulated by the presence of 5×10<sup>-5</sup>% of sodium molybdate (Van Niel, Arch. Mikrobiol. 1935, 6, 215).

### Nitrogen Fixation by *Azotobacter*.

Kostytschew and his colleagues (Compt. rend. 1925, 180, 2070; Z. physiol. Chem. 1926, 154, 1) concluded that the first step in fixation of nitrogen by *Azotobacter* cultures is formation of ammonia. Winogradsky (Compt. rend. 1930, 190, 661) found that *Azotobacter* give rise to ammonia when they are grown on a silica gel containing a lactate or succinate as a carbon source. The conclusion that the ammonia is the first step in nitrogen fixation was opposed by Burk and Horner (Soil Sci. 1936, 41, 81) who decided that the ammonia arises secondarily by oxidative deamination of cell material. Winogradsky (Zentr. Bakt. 1938, II, 97, 399) pointed out that pure cultures of *Azotobacter* cannot break down organic material to ammonia and hence the appearance of ammonia in the pure cultures of this organism indicates a direct reduction of molecular nitrogen. Horner and Burk (Third Comm. Intern. Soc. Soil Sci. Trans. 1939, A, 168), however, still maintain that the nitrogen excretion of pure *Azotobacter* cultures is largely independent of the form of the nitrogen supply (free or combined).

A manometric technique devised by Burk and his colleagues has made it possible to study nitrogen fixation by *Azotobacter* in a more quantitative and reliable manner than has previously been possible (see Burk, J. Physical Chem. 1930, 34, 1174, 1180; Ergelm. Enzymforsch. 1934, 3, 23). Using this technique it was shown that:

1. The respiration of *Azotobacter*, which is extremely high, is greatest at pressures of oxygen below that in air (Meyerhof and Burk, Z. physikal. Chem. 1928, 139, 139; Lineweaver, J. Biol. Chem. 1932, 99, 575). The maximum nitrogen fixation does not occur at the maximum rate of respiration, but at 4-5% oxygen. The efficiency of fixation (ratio of molecules of nitrogen fixed to molecules of oxygen used) increases with decreasing pressure of oxygen.

2. The rate of nitrogen fixation (in the presence of 0.2 atm. O<sub>2</sub>) attains a maximum at 0.5 to 1 atm.; between 0.05 and 0.5 atm. nitrogen the rate of fixation is roughly proportional to its pressure. The proportionality falls as the nitrogen pressure increases.

3. As with *Clostridium*, the presence of utilisable combined nitrogen diminishes the rate of free nitrogen fixation. Inhibition of fixation by *Azotobacter* is complete in the presence of ammonia nitrogen at a concentration of 0.5 mg. N<sub>2</sub>/100 c.c. A similar result is obtained with nitrate.

4. Growth, both in free and combined nitrogen, is optimal at pH 7.6-7.8, that in the former being more sensitive to a drop in pH (Burk, Lineweaver, and Horner, J. Bact. 1934, 27, 325).

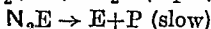


5. Calcium is essential for the fixation, maximum fixation being obtained at  $2 \times 10^{-4}$  M. Calcium may be replaced by strontium (Burk and Lineweaver, Arch. Mikrobiol. 1931, 2, 155). Substances (e.g., fluoride or oxalate) which immobilise the calcium, inhibit the nitrogen fixation.

6. The presence of molybdenum has a highly beneficial effect on *Azotobacter* growth in free nitrogen (first observed by Bortels, Arch. Mikrobiol. 1930, 1, 333). A positive effect of molybdenum on the growth of the organism can be observed at a concentration of 1-3 parts in  $10^{12}$ . Vanadium can replace molybdenum but is less effective.

7. Humus of soil has a beneficial effect on *Azotobacter* growth, the action being due, supposedly, to the presence of iron (Rosing, Zentr. Bakt. 1912, II, 33, 618; Burk, Lineweaver, and Horner, Soil Sci. 1932, 33, 413). It is possible that molybdenum is the responsible factor in humus so far as the effect on nitrogen fixation is concerned.

Burk and his colleagues have postulated that the following enzyme mechanism is responsible for nitrogen fixation in *Azotobacter*:



E refers to a specific enzyme, *nitrogenase*, which combines reversibly with the nitrogen molecule to form the enzyme-substrate complex  $\text{N}_2\text{E}$ . This breaks down irreversibly into E and the products P, which corresponds to an increase in *Azotobacter* cells. The total system responsible for fixation has been termed *azotase*. (Cf. Burk and Horner, Proc. Third Intern. Cong. Microb. 1939, p. 489; Starkey, *ibid.*, p. 142).

#### PHYSICO-CHEMICAL PROPERTIES OF THE SYMBIOTIC NITROGEN FIXING SYSTEM.

Work by Wilson and his colleagues (J. Amer. Chem. Soc. 1936, 58, 1256; Ergebn. Enzymforsch. 1939, 8, 13) has given the following results:

1. The fixation of free nitrogen by inoculated red clover plants is independent of the partial pressure of nitrogen above 0.10-0.15 atm.

2. The fixation of free nitrogen by inoculated clover plants is inhibited by molecular hydrogen. This is not the case with *Azotobacter*. The inhibition appears to be of the competitive type, indicating the possibility that free nitrogen and hydrogen compete for a common catalytic system.

3. If the pressure of oxygen is greater than 0.1 atm. and less than 0.4 atm. assimilation of nitrogen (free or combined) is unaffected by the oxygen tension. If the pressure of oxygen is increased above 0.4 atm., a decrease takes place in the rate of assimilation of nitrogen, free or combined (Wilson and Fred, Proc. Nat. Acad. Sci. 1937, 23, 503). The evidence suggests that oxygen plays only an indirect part in controlling the mechanism of nitrogen fixation in the nodule. Work of Mothes and Pietz (Naturwiss. 1937, 25, 201) suggests the presence of an oxidation product of dihydroxyphenylalanine in the nodule

controlling the oxidation potential, and that the pressure of oxygen, by influencing the rate of formation of this product, may alter the potential and thereby the velocity of nitrogen fixation.

4. Carbon monoxide greatly inhibits symbiotic nitrogen fixation. This ceases in red clover when the carbon monoxide concentration in the atmosphere reaches 0.1%.

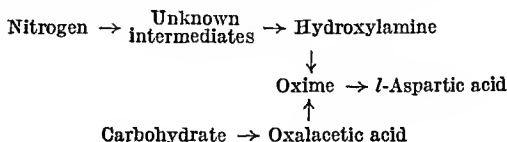
Work of Virtanen (Biochem. Z. 1928, 193, 300) shows that uptake of nitrogen (free or combined) by legumes decreases with increase in acidity. A pH of 5.0 or less inhibits fixation of molecular nitrogen. This may be due not only to the increased hydrogen ion concentration but to the decreased absorption of minerals which takes place at a low pH.

The presence of calcium is important for the development of the legume, but there is no evidence that it is specifically involved in the nitrogen fixing process (Albrecht, Proc. Soil. Sci. Soc. 1937, 2, 315).

Konishi and Tsuga (Mem. Col. Agric. Kyoto, 1936, 20, Chem. Ser. No. 37) have suggested that titanium may be involved in symbiotic nitrogen fixation. A similar suggestion has been made for molybdenum (Bortels, Arch. Mikrobiol. 1937, 8, 13; Bertrand, Compt. rend. 1939, 208, 2024) but the evidence is not conclusive.

#### HYDROXYLAMINE AS A POSSIBLE INTERMEDIATE IN NITROGEN FIXATION.

As stated earlier, the evidence that ammonia is the first product formed in the assimilation of free nitrogen is not yet convincing, and an alternative view that hydroxylamine is among the first intermediates has received more favourable support. This has come from the work of Virtanen, Hausen, and Laine on the excretion of nitrogenous substances by legumes. The experimental evidence of Virtanen and Laine (J. Agric. Sci. 1937, 27, 332; Enzymologia, 1937, 3, 266; Nature, 1938, 141, 748; 142, 165; Biochem. J. 1939, 33, 412) led them to suggest the following scheme as representing the mechanism of symbiotic nitrogen-fixation:



The following relevant data were noted:

1. Cultures of legumes in sterile sand but containing the proper species of *Rhizobia* excrete soluble nitrogenous products apparently only from the nodules, i.e., where fixation of nitrogen takes place. The excreted nitrogen consists almost entirely of *l*-aspartic acid and  $\beta$ -alanine, the latter probably arising from the former by decarboxylation. No ammonia is found.

2. In addition to the two amino acids, 1-2% of the excreted nitrogen consists of an oxime, identified as the oxime of oxalacetic acid,  $\text{HO}_2\text{C}\cdot\text{C}(\text{:NOH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

3. Free oxalacetate is to be found in pea plants actively fixing nitrogen.

4. Excised nodules, intact or crushed, are able to fix atmospheric nitrogen in the presence of

oxalacetate, but cannot do so in its absence, nor when it is replaced by glucose.

So far as excretion of soluble nitrogenous compounds by legumes is concerned it had already been noted by Lipmann (New Jersey Agric. Exp. Sta. Bull. 1912, 253) that non-legumes benefit from association with a legume and it was suggested that this benefit arises from the nitrogenous compounds excreted by the legumes.

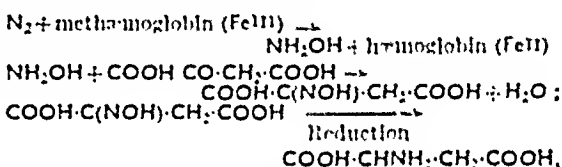
There have been failures to confirm these phenomena and the reader is referred to Perry Wilson (*op. cit.*) for details and references. It seems that repetition of the work of Virtanen and Laine is required on plants grown under different climatic conditions before their conclusions can be fully accepted. Many complicating factors (temperature, light, shade, etc.) influence the nitrogen excretion of legumes, and Wilson points out that the relation between the rates of photosynthesis and nitrogen fixation may be a controlling factor.

It has been reported (Endres, Virtanen, and Laine) that small quantities of aspartic acid and traces of oxalacetic oxime are to be found in *Azotobacter* cultures but doubt has been thrown by Horner and Burk (Third Comm. Intern. Soc. Soil Sci. 1939, A, 168) on the significance of these results.

#### FUNCTION OF THE RED PIGMENT OF NODULES.

A red pigment in the root nodules of a legume (*Vicia faba*) was first investigated by Pietz (Zentr. Bakt. 1938, II, 99, 1), who thought it was identical with the red intermediate product appearing in the enzymic oxidation of tyrosine, and that its function was to poise the oxidation-reduction potential of the nodule at a level favourable for proliferation of *Rhizobia* in the nodule. Kubo later (Acta Phytochim. 1939, 11, 195) concluded that the red pigment of the nodules is a haemoprotein analogous to haemoglobin and that it acts as an oxygen store and carrier. Burris and Haas (J. Biol. Chem. 1944, 155, 227) agreed with Kubo that the pigment is a haemin compound but, contrary to Kubo, did not consider it analogous to haemoglobin. Keilin and Wang (Nature, 1945, 155, 227) found that the pigment of root nodules of the soya bean is a haemoglobin the absorption spectrum of which shows two distinct bands with the maxima at about 574  $m\mu$ . ( $\alpha$ ) and 540  $m\mu$ . ( $\beta$ ), the  $\alpha$ -band being narrower and lower than the  $\beta$ -band. The root-nodule haemoglobin represents the first case of the occurrence of this pigment in plants. Neither the plant cells alone nor the *Rhizobia* grown separately synthesise haemoglobin; apparently the *Rhizobia* supplies a factor to the plant necessary for synthesis of haemoglobin in the nodule. The pigment is present in nodules of all legumes so far investigated, and appears to be associated in some way with symbiotic nitrogen-fixation. Carbon monoxide inhibits symbiotic nitrogen-fixation at the low pressure at which it reacts with haemoglobin. Virtanen (*ibid.* 1945, 155, 747) has given evidence that the red pigment of nodules, a haemoglobin as indicated by Kubo, is involved in symbiotic nitrogen-fixation, and states that one reason for the inability of free living *Rhizobia* to fix atmo-

spheric nitrogen lies in their lack of haemoglobin. He assumes that the reason that an ineffective strain of *Rhizobia* cannot fix nitrogen is the presence of a slimy layer around the bacteria which prevents uptake of oxygen and inhibits the formation of haemoglobin. Virtanen and Laine (*ibid.* 1946, 157, 25) have found that methaemoglobin also exists in root nodules, and that a green pigment may be produced by long standing of the nodules in the dark. The green pigment appears to be due to a breakdown of the porphyrin of haemoglobin. Nitrogen fixation ceases when the nodules become green. According to Virtanen and Laine (*loc. cit.*) the equilibrium between haemoglobin and methaemoglobin depends upon the presence of oxalacetic acid in the plant. Methaemoglobin is reduced to haemoglobin by the action of oxalacetic acid. They have made the following hypothesis relating nitrogen fixation to valency changes in the haemoglobin, with the proviso that the hydroxylamine need not appear directly from the molecular nitrogen but possibly after a number of intermediate stages:



Letche (Z. physiol. Chem. 1912, 80, 412) had already noted that hydroxylamine reacts with oxyhaemoglobin to form haemoglobin and nitrogen.

The position at present concerning symbiotic nitrogen-fixation appears to be that Virtanen's hydroxylamine hypothesis has the greatest weight of experimental evidence in its favour, but that much more work is required for the establishment of the details of the chemical mechanisms involved.

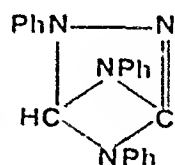
J. H. Q.

NITROGLYCERIN (v. Vol. IV, 491d).

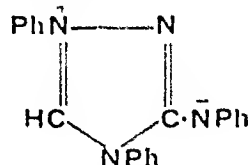
NITROGLYCOL (v. Vol. IV, 489f).

"NITROLIM" (v. Vol. II, 219c; V, 65d; this Vol., p. 553b).

NITRON,  $\text{C}_{20}\text{H}_{16}\text{N}_4$ , mol. wt. 312.15.



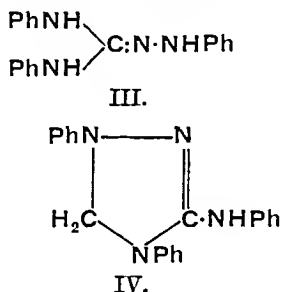
I.



II.

1:4-diphenyl-3:5-endonitrodihydrotriazole (I) discovered by Busch (Ber. 1905, 38, 856) may also be formulated with the betaine structure (II) discussed by Schönberg (J.C.S. 1938, 824). Nitron crystallises in pale yellow needles from organic solvents and has m.p. 189°. It forms many sparingly soluble salts of which the nitrate, picrate, and perchlorate are among the least soluble and have been used for the gravimetric estimation of these acids. The reagent may be prepared as follows: diphenylthiourea (20 g.) is refluxed with 0.5 l. dry benzene and dry mercuric or lead oxido added in small portions so long as a black precipitate is formed; the hot

solution is then filtered, 10 g. phenylhydrazine added and the solution concentrated to 50 c.c. On cooling, if necessary with addition of some light petroleum, triphenylaminoguanidine (III) crystallises out. In the original method (Busch, J.S.C.I. 1905, 24, 289) this substance was heated for 2 hours in a sealed tube at 175° with twice its weight of 90% formic acid (Vol. VI, 150a), the product dissolved in water, the nitron precipitated by ammonia and extracted with chloroform. A method which avoids heating in a sealed tube has been described (Busch and Mehrtens, Ber. 1905, 38, 4055; Desvergnès, Mon. Sci. 1923, [v], 13, 208; Merck, G.P. 161235). Triphenylaminoguanidine, 100 g., is boiled under reflux for  $\frac{1}{2}$  hour with 250 c.c. of alcohol and 100 c.c. of 40% formaldehyde. The product, 1:4-diphenyl-3-anilidodihydrotriazole (IV), is oxidised in acetic acid solution, preferably by addition of aqueous sodium nitrite; nitron nitrite and nitrate crystallise out and are worked up for nitron as described in the first method.



**Nitron Reagent.**—The same solution is used for qualitative and for quantitative analysis; it is prepared by dissolving 10 g. nitron in 100 c.c. of 5% acetic acid. This is sufficient for 8–10 determinations. Small quantities of the reagent may be kept for a short time in dark glass bottles (Pooth, Z. anal. Chem. 1909, 48, 375).

**Detection of Nitrates.**—Five c.c. of the solution under examination are mixed with one drop of dilute sulphuric acid and 5–6 drops of nitron reagent (*v. supra*). If a nitrate is present (1:33,000) a precipitate is formed in 5 hours (Busch and Mehrtens, *l.c.*), or, if the quantity be very small, fine needles separate; 1:60,000 may be detected in 2 hours at room temperature or 1:80,000 at 0° (Busch, Ber. 1905, 38, 861). A precipitate is not characteristic since it is given by the following acids at limits of concentration stated, where known, in parentheses: chloric (1:4,000), chromic (1:6,000), ferricyanic, ferrocyanic, hydriodic (1:20,000), hydrobromic (1:800), nitrous (1:4,000), oxalic, perchloric (1:50,000), picric (1:250,000), salicylic, thiocyanic (1:50,000), thiosulphuric, tungstic. Interfering acid radicals must be removed before making the test; *e.g.*, treatment with chlorine has been used to remove HBr, iodate was found suitable for removing HI, nitrous and chromic acids were decomposed by reaction with solid hydrazine sulphate. There is a conflict of opinion regarding the effect of citric acid (Hes, Z. anal. Chem. 1909, 48, 81; F. Emich, "Mikrochemisches Praktikum," 2te Aufl. 1931, 100; P. von Stein, "Organic Reagents in Inorganic Analysis," 1942, p. 142).

**Determination of Nitrates** (Vol. II, 598c).—It is an advantage of the process that nitron nitrate contains only 16.79%  $\text{HNO}_3$  for there is usually a loss of 1–2 mg. on washing the precipitate. Satisfactory results are nevertheless obtained in the Busch method (Busch, *l.c.*, p. 861; Z. anal. Chem. 1909, 48, 368) and in improvements of the original procedure Heck, Hunt, and Mellon (Analyst, 1934, 59, 18) found no adsorption of reagents in the precipitate such as would contribute to a balancing of errors. These authors adopted Gutbier's method (Z. angew. Chem. 1905, 18, 494) as follows: the solution containing about 0.12 g. nitrate in 80–100 c.c. is acidified with 10–15 drops of sulphuric acid diluted 2:3, heated nearly to boiling and 10–12 c.c. nitron reagent (*v. supra*) added. After cooling to room temperature the beaker is placed in ice-water for 1–1½ hours, the precipitate is then transferred to a filter-crucible, small portions of the filtrate being used to transfer the last traces of the precipitate which is then washed with not more than 12 c.c. iced water in portions of 2–3 c.c. The precipitate is dried at 105–110°, usually for 45 minutes, and weighed as  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HNO}_3$ . Factors: to  $\text{HNO}_3$ , 0.1679; to  $\text{NO}_3$ , 0.1653; to N, 0.0373. Winkler (*ibid.* 1921, 34, 46) acidifies the solution with 1 c.c. glacial acetic acid, allows the liquid and precipitate to stand for 24 hours in the dark at 15–20°, and washes the precipitate with 50 c.c. cold saturated solution of nitron nitrate. The final washing is 3–5 c.c. ice-cold water (Vasilieff, J.C.S. 1910, 98, ii, 1109). The last-named author allows the liquid to stand for 5–8 hours at 0° before filtering. Heck *et al.* (*l.c.*) carried out comparative determinations with 0.1200 or 0.1201 g. alkali nitrate, with the following results: Gutbier-Busch nitron, 0.1191; Vasilieff-Busch nitron, 0.1194; Kolthoff, titrimetric with  $\text{FeSO}_4$ , 0.1193; reduction with Devarda's alloy, 0.1154; Moore, modified Kjeldahl, 0.1142. The nitron method gave satisfactory analyses of metallic nitrates thus confirming earlier work by Collins (Analyst, 1907, 32, 349) and Vasilieff (*l.c.*). Nitrates in presence of a number of inorganic salts have been determined by Gutbier (*l.c.*) and Hes (*l.c.*). Chlorides may interfere; Winkler (*l.c.*) has published a table of corrections. Pooth (*l.c.*) states that hydrochloric acid in the solution should not exceed 100 c.c. N. per 0.1 g. nitrate present.

**Hydrogen peroxide** required as a reagent in the analysis of cellulose nitrate, nitroglycerin, nitromannitol, nitrostarch, and nitrites, may contain nitric acid (Young and Bernays, Ind. Eng. Chem. [Anal.], 1940, 12, 90). Sulphuric or phosphoric acid, often present in hydrogen peroxide, do not interfere in the nitron method.

**Determination of Nitrogen in Cellulose Nitrate.**—This analysis is usually carried out in Lunge's nitrometer but the nitron method is an alternative as shown by Busch and Schneider (Z. ges. Schiess- u. Sprengstoffw. 1906, 1, 232). About 0.2 g. cellulose nitrate is added to 5 c.c. of 30% sodium hydroxide solution and 10 c.c. of 3% hydrogen peroxide. The mixture is heated on the water-bath until frothing ceases and then over the flame until solution is com-

plete. 40 c.c. of water and 10 c.c. of hydrogen peroxide are then added and the liquid is heated to 50°, 40 c.c. of 5% sulphuric acid are introduced beneath the liquid from a pipette and the temperature raised to 80°, 12 c.c. of nitron reagent (*see supra*) are admixed and the beaker allowed to cool. It is then placed in ice-water for 1-2 hours and the nitron nitrate filtered off and weighed as already described. In the absence of hydrogen peroxide some of the nitrate radical is reduced to nitrite with a small quantity of ammonia (E. C. Worden, "Technology of Cellulose Esters," 1921, I, ii, 980; I, iii, 1679, 2316; J.S.C.I. 1908, 27, 715). Compared with the nitrometer method the results were 0.13-0.01% N higher.

**Determination of Nitrogen in Nitroglycerin.**—A tedious process which includes saponification for 24 hours with repeated small additions of 30% hydrogen peroxide (Cope and Barab, J. Amer. Chem. Soc. 1917, 39, 504).

**Determination of Nitrate and Nitrite in mixtures, especially commercial Nitrite.**—Busch (Ber. 1906, 39, 1401) dissolves 0.1-0.2 g. of the sample in a mixture of 50 c.c. of water and 20 c.c. of 3% hydrogen peroxide which is then heated to 70° and 20 c.c. of 2% sulphuric acid introduced beneath the liquid from a pipette, the temperature is raised to 90° and 12 c.c. of nitron reagent added. Following the usual procedure the nitrate originally present together with that formed by oxidation of nitrite is thus estimated. In a second determination a solution of about 0.1 g. of the sample in 5 c.c. of water is slowly dropped on to 0.25 g. of solid hydrazine sulphate contained in a cooled flask. After completed reaction the solution is diluted to 100 c.c. and the nitrate originally present is now estimated as nitron nitrate (*cf.* Oelmer, Z. angew. Chem. 1918, 31, i, 170, 178).

**Determination of Nitrate and Nitrite in bacteriological cultures.**—Franzen and Löhmann (J. pr. Chem. 1909, [ii], 79, 330) adopt Busch's method above described, but when much organic matter is present they add 1 c.c. of conc. sulphuric acid to 100 c.c. of the solution, before precipitation, to prevent the formation of colloidal nitron nitrate.

**Determination of Nitrate in meat extract.**—Paal and Ganghofer (Z. Nahrungs. Genussm. 1910, 19, 322) describe methods of clarifying the extract before precipitation with nitron reagent.

**Determination of Nitrate in soil.**—Litzendorff (Z. angew. Chem. 1907, 20, 2209; *cf.* Seydel and Wichers, *ibid.* 1911, 24, 2046) analysed samples containing 20-30 p.p.m. of nitrogen as  $\text{NO}_3$ .

**Nitrous fumes in air** may be absorbed by alkaline hydrogen peroxide solution in which nitrate is subsequently determined by the nitron method. According to Burrell and Seibert (U.S. Bur. Mines, 1913, Bull. No. 42, 67) the air to be analysed is aspirated into a 5-10 l. bottle containing 10 c.c. each of 5% potassium hydroxide solution and 3% hydrogen peroxide and the bottle is shaken until reaction is complete. The liquid and washings are then transferred to a beaker and should not exceed 30-40 c.c. After acidifying with dilute sulphuric acid nitron nitrate is determined with the usual precautions. Results are satisfactory; 0.2 c.c.

and 3.7 c.c. of nitric oxide measured into the bottle yielded precipitates equivalent respectively to 0.2 c.c. and 3.5 c.c. For a similar method but with continuous aspiration, *see* E. Berl, "Chem.-tech. Untersuchungsmethoden," 8te Aufl. 1932, II, i, 422.

**Nitrates in water**, if not less than 100 mg. per l., an unusually high amount, may be estimated with nitron (Busch, Z. anal. Chem. 1909, 48, 370).

**Determination of Picric Acid**, (i) as nitron picrate, (ii) as nitron nitrate. In the first method (Busch and Blume, Z. angew. Chem. 1908, 21, 354) 150 c.c. of a solution of about 0.15 g. of picric acid are mixed with 1-2 c.c. of dilute sulphuric acid, heated to nearly boiling and 10 c.c. of nitron reagent (*v. supra*) added. After cooling to room temperature the precipitate is collected on a filter-crucible, washed with 50-100 c.c. of cold water, dried at 110°, and weighed. (Factor to picric acid, 0.4232; trinitroresol is determined similarly, factor, 0.3873.) In presence of sulphuric acid, phenol and the mono- and di-nitro phenols give no precipitate with nitron (Cope and Barab, *l.c.*; Desvergues *l.c.*). Utz (Z. anal. Chem. 1908, 47, 140) obtained less convincing results by oxidative hydrolysis of picric acid in method (ii).

**Determination of Perchlorate.**—This estimation was described by Cope and Barab (*l.c.*) and was adapted to the analysis of Chili saltpetre by Värtheim (Rec. trav. chim. 1927, 46, 97). The solution of the sample is rendered strongly alkaline and treated with Devarda's alloy until nitrate and chlorate are reduced; it is then acidified with acetic acid and nitron perchlorate,  $\text{C}_2\text{O}_5\text{H}_4\text{N}_2\text{HClO}_4$ , precipitated by addition of nitron reagent. The precipitate is allowed to stand for 24 hours before filtering. Washing and drying are carried out as in the determination of nitrate (Storm, U.S. Bur. Mines, 1916, Bull. No. 96, 65).

**Determination of Chloric Acid.**—Hes, *l.c.*; Cope and Barab, *l.c.*

**Nitron Salts of Less Common Acids** have been prepared for characterisation, *e.g.*, fluorophosphoric (Lange, Ber. 1927, 60 [B], 962); fluorosulphonic (Traube *et al.*, Ber. 1921, 54 [B], 1618); hexafluoroantimonic, hexafluoroarsenic, hexafluorophosphoric (Lange *et al.*, *ibid.* 1930, 63 [B], 1058), trifluoroacetic (Swarts, Bull. Soc. chim. Belg. 1930, 48, 190).

**Detection of Rhenium.**—A microchemical test employing nitron is described by Kronmann and Bibikova (A. 1933, 138).

**Determination of Rhenium.**—As nitron perchlorate (Vol. II, 611a; Young and Bernays, *l.c.*, I. Mellan, "Organic Reagents in Inorganic Analysis," 1941, 71).

**Determination of Tungstic Acid.**—Guthrie and Weiso (Z. anal. Chem. 1914, 53, 426) dissolve about 0.15 g. of the acid in sufficient concentrated sodium hydroxide solution, dilute with hot water to 150 c.c., acidify with acetic acid, boil, and add nitron reagent. The precipitate after washing with the diluted reagent (4:98) is ignited and weighed as  $\text{WO}_3$ .

**Recovery of Nitron from Precipitates and Filtrates.**—The base is liberated by addition of 5% ammonia, washed, dissolved in

dilute acetic acid, reprecipitated with ammonia, washed and dried *in vacuo*. The operations are carried out in semi-darkness and preferably in an inert atmosphere (Collins, *l.c.*; Cope and Barab, *l.c.*).

**Substitutes for Nitron.**—Organic bases yielding nearly insoluble nitrates have been described but have not been developed into routine reagents, they include cinchonamine (Vol. III, 152a; Howard and Chick, *J.S.C.I.* 1909, 28, 53), di( $\alpha$ -naphthylmethyl)amine (Rupe and Becherer, *J.C.S.* 1923, 124, ii, 577), "for-nitral" (Vol. V, 327) which is a salt of nitron.

*Nitron as accelerator in the vulcanisation of rubber.*—Roman, *Chem. Zentr.* 1924, I, 2547.

J. N. G.

**NITROPHENINE YELLOW.** A direct cotton dyestuff formerly prepared by coupling diazotised *p*-nitroaniline with dehydrothio-*p*-toluidinesulphonic acid and optionally also with primuline; it gives yellow shades which are not fast to light, alkalis or acids.

J. N. G.

**NITROPHENOLS AND THEIR HOMOLOGUES.** *o*-Nitrophenol.—If oxidation and formation of tarry materials are to be avoided the nitration of phenol must be carried out under very mild conditions, when the reaction is not directly comparable to normal aromatic nitration. The presence of small amounts of nitrous acid is essential; this is not explained simply by the formation of nitroso-phenols followed by their oxidation regenerating nitrous acid, since approximately equal proportions of *o*- and *p*-nitrophenols are produced instead of mainly the *para*-. The reaction must proceed via two complexes between phenol and nitrous acid, which are decomposed oxidatively at different rates (Veibel, *Ber.* 1930, 63 [B], 1577, 1582, 2074; *Z. physikal. Chem.* 1930, B 10, 22). Beaucourt and Hämmerle (*J. pr. Chem.* 1928, [ii], 120, 185) allow phenol, liquified by water, acetic acid or alcohol, to drop into well-stirred nitric acid of  $\rho$  1.35 at 8° over a period of 1½ hours. Steam distillation yields 40% of *o*-nitrophenol, leaving an almost equal quantity of the *para*-isomer. Some 2.5% of 2:4-dinitrophenol is also produced. Increasing the density of the acid to 1.42 gives rather more *para*-, whilst a temperature of 16–20° gives more *ortho*-. 25% of the *ortho*-compound and 60% of the *para*- may be obtained using acid of density 1.4 at 15° in chloroform (Baroni and Kleinau, *Monatsh.* 1936, 68, 251). Other nitrating agents, benzoyl (Francis, *Ber.* 1906, 39, 3798) and acetyl nitrate (Pictet and Khotinsky, *ibid.* 1907, 40, 1163), may be used in the laboratory with sacrifice of convenience. Nitrogen dioxide reacts smoothly in organic solvents giving rather more *para*- than *ortho*-compound (Wieland, *ibid.* 1921, 54 [B], 1780; Monti, *Gazzetta*, 1937, 67, 628).

*o*-Nitrophenol may also be prepared from the corresponding chloronitrobenzene (Engelhard and Latschinow *Z. für Chem.* 1870, 231) and from nitrobenzene (Wohl, *G.P.* 116790; *Ber.* 1899, 32, 3486) by treatment with caustic alkali. It forms yellow needles, m.p. 45°, b.p. 216°, sparingly soluble in cold water, easily in hot alcohol and ether, and readily volatile in steam.

*m*-Nitrophenol, prepared via the diazotisation of *m*-nitroaniline (Manske, "Organic Syntheses," 1928, 8, 80), has m.p. 97°, b.p. 194°/70 mm. It is very soluble in alcohol and ether, and non-volatile in steam.

*p*-Nitrophenol is produced simultaneously with the *ortho*-compound in the processes already described for the nitration of phenol. A useful special method is the oxidation of *p*-nitrosophenol (Robertson, *J.C.S.* 1902, 81, 1477; Boslovskii and Mamutov, *Khim. Referat. Zhur.* 1940, No. 2, 27). It has m.p. 114°, is very soluble in alcohol, ether, and hot water, and non-volatile in steam. Seaman, Norton, and Sundberg (*Ind. Eng. Chem. [Anal.]*, 1940, 12, 403) describe a technique for the determination of *o*-nitrophenol as an impurity by fluorescence analysis after reduction and reaction with benzoic acid.

**2:4-Dinitrophenol.**—The literature concerning this compound is reviewed and the processes of its manufacture from 2:4-dinitrochlorobenzene and from phenol described in detail by Desvergnès (*Chim. et Ind.* 1931, 26, 507, 1271; 1932, 27, 278, 527). Shorygin, Topchiev, and Anan'ina (*J. Gen. Chem. Russ.* 1938, 8, 986) claim that 76% of 2:4-dinitrophenol may be obtained directly from phenol using liquid nitrogen peroxide, provided that the highly exothermic reaction be moderated by maintaining at 0°. Zakharov (*J. Chem. Ind. Russ.* 1927, 4, 960; 1928, 5, 26; 1929, 6, 698), has examined the mercury-catalysed nitration and oxidation of benzene (Wolfenstein and Bötters, *G.P.* 194883; *Ber.* 1913, 46, 588). He finds that catalyst solutions which yield initially only 40% of the product can give up to 80% after repeated use, and thus a continuous process is desirable. The reaction temperature is between 20° and 30°. Bradner and Beall (*U.S.P.* 1723761) also describe a continuous process in which nitrogen peroxide, oxygen, and benzene are fed into the agitated reaction mixture of mercury catalyst and acetic acid. The nitric acid concentration is kept at 45–50%. It forms practically colourless crystals of m.p. 114°, soluble in organic solvents and steam volatile.

**2:4:6-Trinitrophenol v. PICRIC ACID** (Vol. IV, 476b).

**4:6-Dinitro-2-aminophenol (Picramic Acid)** is prepared by partial reduction of picric acid by sodium sulphide (Brand, *J. pr. Chem.* 1906, [ii], 74, 472), hyposulphite (Seyewetz and Blanc, *Chim. et Ind.* 1930, 25, 605; Clayton, *J. Soc. Dyers and Col.* 1930, 46, 365) or iron and salt (Lyons and Smith, *Ber.* 1927, 60 [B], 181). It has m.p. 169°, is soluble in benzene, acetic acid, and alcohol, and sparing so in ether and water.

**Nitrocresols.**—The existing methods of preparation of the ten mono-nitrocresols are discussed critically, and improvements described by Clemence and Raiziss (*J. Amer. Pharm. Assoc.* 1934, 23, 563). Other references are given in the table shown on the opposite page.

**Nitroxyleneols.**—Rowe *et al.* (*J.S.C.I.* 1930, 49, 469r; 1931, 50, 79r) describe the nitration of xyleneols.

**Nitroresorcinols.**—The preparation of 2- and 4-mononitroresorcinols by direct nitration

Compound.	M.p.	Preparation.	Ref.
3-Nitro-2-cresol .	70°	Nitration of <i>o</i> -cresol.	1
4-Nitro-2-cresol .	118°	Nitration and demethylation of <i>o</i> -toluidine.	2
5-Nitro-2-cresol .	96°	Nitration of <i>o</i> -cresol.	1
2-Nitro-3-cresol .	41°	Nitration of <i>m</i> -cresol.	3
		Nitration of sulphonated <i>m</i> -cresols.	4
4-Nitro-3-cresol .	56°	Nitration of <i>m</i> -cresol.	5, 6
		Amyl nitrite on <i>m</i> -cresol.	7
5-Nitro-3-cresol .	90-91°	From 5-nitro-3-toluidine.	8
6-Nitro-3-cresol .	129°	Nitration of <i>m</i> -cresol.	5, 6
2-Nitro-4-cresol .	70°	From 2-nitro-4-toluidine.	9
3-Nitro-4-cresol .	36.5°	Nitration of <i>p</i> -cresol.	10
3:5-Dinitro-2-cresol	86.5°	Nitration of <i>o</i> -cresol.	1, 6, 7, 11
		From dibromo- <i>o</i> -cresol.	12
		From disulphonated <i>o</i> -toluidine.	13
4:6-Dinitro-3-cresol	101°	Nitration of <i>m</i> -cresol.	14
2:3-Dinitro-4-cresol	150°	Nitration of 2-nitro-4-cresol.	15
3:5-Dinitro-4-cresol	84°	Mercuric chloride, sodium hydroxide on 3:5-dinitrotoluene.	16
		Nitration of <i>p</i> -cresol.	17

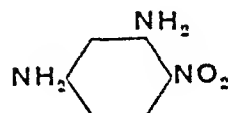
- 1 Gibson, J.C.S. 1925, 127, 44.
- 2 Ullmann and Flitzenbam, Ber. 1905, 38, 3704.
- 3 Gibson, J.C.S. 1923, 123, 1271.
- 4 Hodgson and Beard, *ibid.* 1925, 127, 498.
- 5 Khotinsky and Jacopson-Jacopmann, Ber. 1900, 42, 397.
- 6 Baroni and Kleinau, Monatsht. 1936, 68, 251.
- 7 Ajello and Sigalla, Gazzetta, 1930, 69, 67.
- 8 Neville and Wither, Ber. 1882, 15, 2986.
- 9 Harvey and Robson, J.C.S. 1938, 60.
- 10 Frye and O'Neal, U.S.P. 2136187.
- 11 Bovini, Amer. Chem. Abstr. 1929, 22, 1578.
- 12 Bures, *ibid.* 1928, 22, 63.
- 13 Datta and Varma, J. Indian Chem. Soc. 1927, 4, 321.
- 14 Shorygin, Topehlev, and Anan'ina, J. Gen. Chem. Russ. 1933, 8, 986.
- 15 Dadsell and Kenner, J.C.S. 1927, 580.
- 16 Hodgson and Smith, *ibid.* 1930, 2035.
- 17 Monti, Gazzetta, 1937, 67, 628.

ofresorcinol is described by I.G. Farbenind. A.-G. (G.P. 633982) and Hodgson and Dyson (J.C.S. 1935, 948).

2:4:6-Trinitroresorcinol (*Styphnic Acid*) is prepared by adding resorcinol portionwise to sulphuric acid at 40°, heating the resulting solution on the steam bath, cooling to 0° and nitrating. On pouring into water the product crystallises (Morz and Zetter, Ber. 1879, 12, 2037; Sah, Amer. Chem. Abstr. 1932, 26, 5927). Industrially, a similar process (Wilkinson, U.S.P. 2246963), or, alternatively, the nitration of dinitroresorcinol (Jones and Roberts, U.S.P. 2301912) may be employed. Styphnic acid forms yellow needles from ethyl acetate, m.p. 179-180° which explode on rapid heating; it is soluble in alcohol and ether, and sparingly so in water. It is useful for the identification of aromatic hydrocarbons (Brass and Fanta, Ber. 1936, 69 [B], 1) and alkaloids as their molecular complexes.

G. W. K.

# 4-NITRO-*m*-PHENYLENEDIAMINE, C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>N<sub>3</sub>,



obtained from diformyl-*m*-phenylenediamine which is nitrated to give the 3-nitro-derivative from which the formyl groups are then removed, yield ca. 90% (Gordonov, B. 1934, 792); also prepared by heating 4-nitroaniline-3-sulphonic acid with ammonia to 180° (Agfa, G.P. 130438). It forms yellowish-red prisms with a blue reflex, m.p. 161°. It is used as a coupling component in a number of fast dyestuffs for cotton, e.g., Pyramine Orange 3G, R, and 2R, and also for dyeing fur and feathers (G.P. 262692).

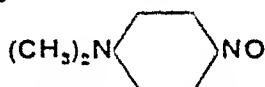
J. N. G.

## NITROSO-COLOURING MATTERS

are derived from nitroso-phenols (quinoneoxime, v. *p*-NITROSOPHENOL) by forming their coloured insoluble co-ordination compounds containing iron, chromium, cobalt, or nickel, e.g., Naphthol Green B, the complex ferric sodium salt of 1-nitroso-2-naphthol-6-sulphonic acid (cf. Vol. I, 263a; III, 335c). These compounds may be precipitated for use as pigments or the reaction may take place on a suitably prepared fabric to give a dyed material. Corresponding copper (Vol. II, 586b) and cobalt (Vol. II, 552d, 578a, 612c) compounds of oximes are utilised in analytical separations.

J. N. G.

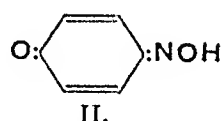
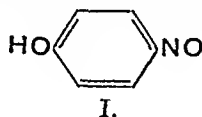
# *p*-NITROSODIMETHYLANILINE, C<sub>8</sub>H<sub>10</sub>ON<sub>2</sub>,



prepared by adding a concentrated solution of sodium nitrite to a strongly cooled solution of dimethylaniline in 20% hydrochloric acid, when the hydrochloride separates as yellow crystals, m.p. 177° (decomp.). The free base, green leaflets from ether, has m.p. 92.5-93.5°. Reduction with tin and hydrochloric acid gives NN-dimethyl-*p*-phenylenediamine. It is an intermediate for many dyestuffs, e.g., it condenses with β-naphthol to give Meldola's Blue, cf. CAPRI BLUE.

J. N. G.

# *p*-NITROSOPHENOL (I), or *p*-benzo-quinone monooxime (II),

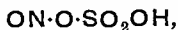


Yellowish needles, decompose at 124°. The same compound is precipitated in two reactions which are related respectively to the two formulæ: (I) by the interaction of phenol, potassium nitrite, and acetic acid, and (II) from quinono and hydroxylamino hydrochloride. For metallic salts of oxime structure (II), v. NITROSO-COLOURING MATTERS (v. *supra*).

J. N. G.



**NITROSULPHURIC ACID.** Saltpeterschwefelsäure (Germ.), an old name for an acid assumed to exist in mixtures of concentrated nitric and sulphuric acids; its salts termed nitratosulphates are known, e.g., the mineral *darapskite*,  $\text{Na}_2\text{SO}_4 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$ . A related compound is nitrosylsulphuric acid,



cf. Elliott *et al.*, J.C.S. 1926, 1219; J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, 1922, pp. 691, 816; Vol. VIII, 1928, p. 696.

J. N. G.

**NITROSYLS, METAL.** Metal nitrosyls may be defined as compounds the molecules of which contain one or more nitrosyl (NO) groups directly bonded to a metal atom. The number of known compounds of this type is not large, and their formation is largely characteristic of the group of elements comprising iron, cobalt, nickel, and the platinum metals; these are also typical carbonyl-forming elements (*v.* CARBONYLS, Vol. II, 357*a*), and the nitrosyls and carbonyls are closely related classes of compounds.

Metal nitrosyls containing no group other than NO attached to the metal atom are not well established compounds; in this respect the nitrosyls differ, as a class, from the carbonyls, for a number of carbonyls contain metal atoms bonded to CO groups only (cf. Welch, Chem. Soc. Annual Rep. 1941, 38, 71). The existence of a cobalt nitrosyl,  $\text{Co}(\text{NO})_3$ , has been reported (Hieber, Angew. Chem. 1936, 49, 463; G.P. 613400, 613401, 1932), but full details of its preparation and properties are not available; if its existence is confirmed, this compound will provide the first authentic example of an unsubstituted metal-nitrosyl. Supposed "nitrosyls" of iron [ $\text{Fe}(\text{NO})_4$ , Manchot and Enk, Annalen, 1929, 470, 275] and ruthenium [ $\text{Ru}(\text{NO})_4$  or  $\text{Ru}(\text{NO})_5$ , W. Manchot and W. J. Manchot, Z. anorg. Chem. 1936, 226, 410] may contain nitrosyl groups, but their constitution is open to question, and they are probably not simple nitrosyls; the iron compound has been formulated as a hyponitrite,  $[\text{Fe}(\text{NO})_2]\text{N}_2\text{O}_2$ . It is noteworthy that the cobalt compound,  $\text{Co}(\text{NO})_3$ , is allowed for by the general structural principles applying to most of the simpler nitrosyls and carbonyls, but that the supposed iron and ruthenium compounds cannot be formulated in any simple way.

**Nitrosyl Carbonyls.**—The nitrosyl carbonyls of iron and cobalt,  $\text{Fe}(\text{CO})_2(\text{NO})_2$  and  $\text{Co}(\text{CO})_3\text{NO}$ , are volatile compounds which establish the close link between the carbonyls and the nitrosyls. Both form red liquids. The iron compound, m.p.  $18.4^\circ$ , b.p. *ca.*  $110^\circ$ , is prepared (Hieber and Anderson, *ibid.* 1932, 203, 238) by the action of nitric oxide on iron tetra- or ennea-carbonyl (Vol. II, 358*a*). The cobalt compound, m.p.  $-1.1^\circ$ , b.p.  $78.6^\circ$ , is similarly obtained from cobalt tetracarbonyl (Vol. II, 358*c*), but other methods of preparation are also available; in one of these carbon monoxide is passed into an alkaline solution of a cobalt salt, containing cysteine, which is afterwards acidified; nitric oxide is then passed into the solution,

and cobalt nitrosyl carbonyl is evolved as vapour (Coleman and Blanchard, J. Amer. Chem. Soc. 1936, 58, 2160; Blanchard and Gilmont, *ibid.* 1940, 62, 1192). Alternatively, carbon monoxide may be absorbed in an alkaline suspension of cobalt cyanide or sulphide, and nitric oxide passed into the resulting solution (Blanchard, Rafter, and Adams, *ibid.* 1924, 56, 16). Some reactions of the nitrosyl carbonyls of iron and nickel have been studied by Hieber and Anderson (Z. anorg. Chem. 1933, 211, 132).

On structural grounds, nickel might be expected to form a nitrosyl carbonyl of formula  $\text{Ni}(\text{NO})_2\text{CO}$ , but this has never been isolated. The action of nitric oxide on slightly moist nickel carbonyl, in an inert solvent or in the absence of a solvent, affords the hydroxide,  $\text{Ni}(\text{NO})\text{OH}$ , of the univalent  $\text{Ni}(\text{NO})$  radical; other closely related compounds are formed in the presence of an alcohol (Anderson, *ibid.* 1936, 229, 357; Frazer and Trout, J. Amer. Chem. Soc. 1936, 58, 2201). By analogy with iron and cobalt, formation of nitrosyl carbonyls of ruthenium and osmium [ $\text{Ru}(\text{CO})_2(\text{NO})_2$  and  $\text{Os}(\text{CO})_2(\text{NO})_2$ ] and of rhodium and iridium [ $\text{Rh}(\text{CO})_3\text{NO}$  and  $\text{Ir}(\text{CO})_3\text{NO}$ ] may also be predicted. These compounds have not yet been reported, but recent progress in the study of the carbonyl chemistry of these elements fully confirms their close analogy to iron and cobalt.

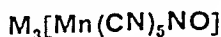
Like the carbonyls, the nitrosyl carbonyls give rise to a number of complex derivatives containing amine or other groups co-ordinated to metal atoms (*see* Hieber and Anderson, Z. anorg. Chem. 1933, 211, 132; H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," London, 1938, Chap. XII).

**Metal Nitrosyl Halides and Other Nitrosyl Derivatives.**—Among other simple metal nitrosyls are the nitrosyl halides of cobalt, of formula  $\text{Co}(\text{NO})_2\text{X}$ , X being a halogen atom. These compounds are prepared by the direct action of nitric oxide on the anhydrous cobalt halides at about  $60^\circ$  (Hieber and Marin, Z. anorg. Chem. 1939, 240, 241). The iodide reacts most readily, giving the nitrosyl compound as dark brown, or black, shining crystals; with the bromide or chloride the reaction is complete only in presence of a halogen-acceptor, such as metallic zinc or cobalt, which combines with the halogen set free in the formation of the nitrosyl. These nitrosyl halides are very stable, and can be sublimed without decomposition. Iron gives formally similar compounds of the type  $\text{Fe}(\text{NO})_2\text{X}$  (Manchot and Fischer, Dissertation, Munchen, 1937). A group of "nitrosyl mercaptides" is known which is clearly related to the nitrosyl halides, and includes compounds of the types  $\text{Fe}(\text{NO})_2\text{SR}$ ,  $\text{Co}(\text{NO})_2\text{SR}$ , and  $\text{Ni}(\text{NO})\text{SR}$ , R being an alkyl group (Reihlen *et al.*, Annalen, 1927, 457, 71; 1928, 465, 72; 1929, 472, 268; 1930, 482, 161; Manchot and Davidson, Ber. 1929, 62 [B], 681). Roussin's salts (*v.* Vol. VII, 60*c*), particularly the red salts of the type  $\text{Fe}(\text{NO})_2\text{SM}'$ , are of a similar group.

Nitrosyl halides in which the nitrosyl group functions as a co-ordinated addendum in complexes of more familiar constitution include  $\text{M}[\text{RuCl}_5\text{NO}]$ , well known in ruthenium

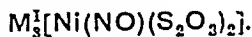


chemistry (Manchot and Schmid, Z. anorg. Chem. 1933, 216, 99), and the analogous osmium compounds,  $M_2^I[OsCl_5NO]$  (P. Pascal, "Traité de Chimie Minérale," Vol. XI, Paris, 1932, p. 370). Closely related to these halides are complex cyanides, of which the "nitroprussides,"  $M_2^I[Fe(CN)_5NO]$  (v. Vol. III, 477a), and the similar compounds  $M_2^I[Fe(CN)_5NO]$  (Manchot and Woring, Ber. 1912, 45, 2869; 1913, 46, 3514), are familiar examples. Other complex nitrosyl cyanides include



(Manchot and Schmid, *ibid.* 1926, 59 [B], 2360),  $M_2^I[Ni(CN)_3NO]$  (Manchot, *ibid.* p. 2448), and  $M_2[Ru(CN)_5NO]$  (Manchot and Düsing, *ibid.* 1930, 63 [B], 1226).

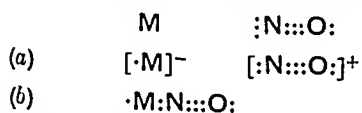
Association of nitrosyl and thiosulphate groups is found in the cobalt nitrosyl thiosulphates,  $M_3^I[Co(NO)_2(S_2O_3)_2]$  (Manchot *et al.*, *ibid.* 1926, 59 [B], 2445; 1929, 62 [B], 681) and in related compounds of iron and nickel,  $M^I[Fe(NO)_2(S_2O_3)]$  and



An iron nitrosyl sulphate,  $Fe(NO)SO_4$  (v. Vol. VII, 58b) finds application in the "brown ring" test for nitrates (v. Vol. II, 572c), and in the purification of nitric oxide; it is an unstable brown substance. The corresponding selenate,  $Fe(NO)SeO_4$ , has been isolated as a crystalline solid (Manchot *et al.*, Annalen, 1910, 372, 165; Ber. 1914, 47, 1601; Z. anorg. Chem. 1924, 140, 37).

For some other more complex nitrosyl derivatives of metals, see Emeléus and Anderson, *op. cit.*, and Welch, Chem. Soc. Annual Rep. 1941, 38, 71.

**Valency Relations in Metal Nitrosyls.**—The constitution of the more complex metal nitrosyls still remains to be established, but the simpler compounds of the group can be formulated satisfactorily if it is assumed that attachment of a nitrosyl group to a metal atom involves donation of three electrons from the nitrogen atom to the metal. This process may be considered to take place in two stages: (a) loss of one electron from the NO group, and incorporation of this electron into the electron orbits of the metal atom; and (b) attachment of the resulting positively charged  $[NO]^+$  group to the metal by an ordinary co-ordinate bond (v. Vol. IV, 273b), the nitrogen atom donating two further electrons to the metal, as below.

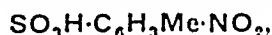


(The metal atom is here shown without regard to its total charge, or to the presence of other attached groups, and nitric oxide is formulated without any attempt to show its resonance structure.) The nitrosyl carbonyls, particularly, are convincingly formulated on this basis, the metal atoms in their molecules reaching the "rare-gas structure" which is believed to be

attained in all simple carbonyls. The structures of iron and cobalt nitrosyl carbonyls, as determined by electron diffraction, are also in accord with the mode of bonding just described (Brockway and Cross, J. Chem. Physics, 1935, 3, 828; Brockway and Anderson, Trans. Faraday Soc. 1937, 33, 1233). For further information on the constitution of nitrosyls (and also carbonyls), see Blanchard, Chem. Reviews, 1940, 26, 409.

A. J. E. W.

#### 4-NITROTOLUENE-2-SULPHONIC ACID, *p*-nitrotoluene-*o*-sulphonic acid,



obtained by sulphonating *p*-nitrotoluene with fuming sulphuric acid at 100° (Kastle, Amer. Chem. J. 1910, 44, 484) crystallises from water in plates, with  $2H_2O$ , m.p. 133.5°, soluble in alcohol, ether, and acetone. The aqueous solution turns deep red when warmed with sodium-hydroxide solution and a series of stilbene dyestuffs (Vol. IV, 221a) is formed by alkaline condensation under varied conditions.

J. N. G.

**NITROTOLUIDINES.** McGookin and Swift (J.S.C.I. 1939, 58, 152) have investigated the nitration of acetotoluidides and obtained the following yields of nitroacetotoluidides, which may subsequently be hydrolysed: from acet-*o*-toluidide, 33% of 3-nitro-, 27% of 4-nitro-, 28% of 5-nitro-; from acet-*m*-toluidide, 16% of 4-nitro-, 65% of 6-nitro-, from acet-*p*-toluidide, 83% of 3-nitro-, 5.9% of 3:5-dinitro-. The last reaction is also described by Biswell and Wirth (U.S.P. 2128511). The preparation of 2- and 5-nitro-*m*-toluidines has been carried out by reduction of 2:3- and 3:5-dinitrotoluene by stannous chloride (Barton and Kenner, J.C.S. 1921, 119, 1017) and ammonium sulphide (Morton and McGookin, *ibid.* 1931, 910), respectively. Morton and McGookin (*loc. cit.*) describe the absorption spectra of all ten mononitro-toluidines.

McGookin (J.S.C.I. 1941, 60, 297) has recently described the preparation of 3:5-, 3:6-, and 5:6-dinitro-*o*-toluidines.

G. W. K.

**NJIMO WOOD.** *Opebe*. *Egbesi* from *Sarcocophalus esculentus* (Fam. Rubiaceae) a tree growing in tropical W. Africa, has been used for furniture and parquet flooring (Chevalier, Rev. Bot. Appl. 1938, 18, 176). The wood yields a yellow bitter extract formerly considered to possess febrifuge properties. The bark and root ("Peach root") were exported to Franco and believed to be substitutes for cinchona bark since they are used for this purpose in native medicine. The presence of the alkaloid "doundakine" in the bark (Bochefontaine *et al.*, Compt. rend. 1883, 97, 271) has been denied (Heckel and Schlagdenhauffen, *ibid.* 1885, 100, 69; Bull. Imp. Inst. 1915, 13, 46). The leaves contain traces of an alkaloid (Boorsma, Bull. Inst. bot. Buitenzorg, 1902, 14, 25). The yellow dyestuff from the wood has no importance for European practice (Dalziel, "Useful Plants of West Tropical Africa," Crown Agents for the Colonies, London, 1937, 411). Oberdoerffer (Tropenpflanzer, 1938, 41, 25) has

"Niobium" is used in British publications usually and "columbium" in American publications. It has not been considered worth while to attempt to standardise the names of the elements for language differences as the words are too common and too well established. A few of the isotopes have been given names, as by use of the prefix radio-. Completely different names for isotopes are deuterium and tritium for  $^2\text{H}$  and  $^3\text{H}$ .

The unsystematic names frequently possessed by compounds are called "trivial" names (German *Trivialnamen*) for lack of a better designation. In the early days such names were often long, as "powder of the Count of Palma" for magnesium carbonate, but in more recent times short, single-word trivial names have been usual. These names play a useful rôle, as many systematic names are inconveniently long and unnecessary for most uses. Moreover, many trivial names serve as stem words for systematic names of derivatives and they may suggest source, a property or the like. Often when a compound first needs a name not enough is known about it for systematic naming to be possible.

Numerous examples of unnecessary and troublesome duplications of names are still encountered to-day. However, in systematic nomenclature there are often several possibilities for a given compound, particularly a complex compound, no one of which is necessarily best. Since the names are systematic this situation does not present a serious problem and may even have advantages, as in teaching and in presenting different relationships or points of view. Organic compounds of mixed function may be given names in which any one of the functions is chosen to dominate. Even among the simpler inorganic compounds there are different possibilities of systematic naming; these do not present serious difficulty. Examples of this influence of differences in point of view or in system of naming will be brought out later.

A very broad influence on nomenclature which may be attributed to point of view lies in the fact that chemistry, as indeed life itself, is largely based on water. Aqueous systems are the common kind studied in chemistry and thinking is in terms of them. We live in a water world. E. C. Franklin has shown that compounds dissolved in liquid ammonia behave in such a way as to justify, from that viewpoint, an entirely different nomenclature from the one developed from the use of water as the common solvent. Indeed, Franklin pointed out (*J. Amer. Chem. Soc.* 1924, 46, 2137-51) that not only oxygen, but also sulphur, nitrogen, the halogens and, to a recognisable extent, even carbon, are acid-, base-, and salt-forming elements in the original Lavoisierian sense under proper conditions as to solvent. In an imaginary ammonia world the amides, imides, and nitriles of the basic metals would be the bases and  $\text{NH}_2\text{Cl}$ ,  $\text{H}_2\text{NCN}$ , or  $\text{HNC}(\text{NH}_2)_2$ ,  $\text{HN}_3$ ,  $\text{H}_2\text{NI}$ ,  $\text{HNSi}(\text{NH}_2)_2$ , and  $(\text{HN})_2\text{PNH}_2$  would be acids (ammono-hydrochloric, -carbonic, -nitric, -hypoiodous, -silicic, and -phosphoric acids, respectively). The alcohols of such a

world would be primary and secondary amines according to our nomenclature and phenol would be aniline. The ethers would be the tertiary amines. Franklin's nomenclature for compounds from that viewpoint is at least of academic interest.

A strong influence in the development of systematic chemical nomenclature has been the requirement of indexes for system in the listing of compounds. This has led to much useful work by editors, done in order that the indexes for which they are responsible might serve as an effective key to the literature concerning the compounds recorded. An abstract journal covering the chemical literature of the world may have occasion to index as many as 25,000 compounds in a year and anything less than the use of rigidly systematic names for these compounds could not help but result in a confusing subject index, with scattered entries and impaired usefulness. What is true of annual indexes is still truer of collective indexes, such as those of the *Zeitschrift für anorganische und allgemeine Chemie*, *British Chemical and Physiological Abstracts*, *Chemical Abstracts*, and *Chemisches Zentralblatt*. The introductions to such publications often contain valuable information for the student of chemical nomenclature.

Aside from their work with indexes, the editors of the numerous scientific and technical journals have a real responsibility in the control of the nomenclature used in their publications. They have to deal with the product of many workers, some of whom are uninformed or not sufficiently careful in regard to the words which they use. This responsibility has been recognised by the frequent inclusion of editors on the nomenclature committees of national chemical societies and of the International Union of Chemistry. Directions for authors and abstractors issued by journal editors are another helpful source of information on nomenclature.

**Other General Considerations.**—An effective device commonly used in chemistry has been the use of significant endings in the names for chemical substances, with classification as the chief objective. This has been done to a limited extent for the elements, as with the *-ium* ending much used in the more recently named metals and of *-on*, as in the names of the inert gases. The *-on* ending has also been used by physicists and chemists in the naming of ultimate particles, as in magneton, proton, deuteron, and photon. A more effective use of significant endings, however, has been in the naming of compounds. The use of the endings *-ide*, *-ite*, *-ate*, *-ous*, and *-ic* in inorganic chemistry will be discussed later, as will also the use in organic chemistry of such endings as *-ano*, *-ine*, *-ol*, and *-yl*.

It is natural that different forms of a well-known substance should receive individual trivial names, as charcoal, graphite, and diamond, or chalk, marble, Iceland spar, etc. Mineralogists have their own names for native chemical compounds, customarily using the ending *-ite*; as, sphalerite for native zinc sulphide, or calcite and aragonite for two different crystal forms of native calcium carbonate.

Chemistry has had industrial applications from early times, starting principally with metallurgy. The application of chemistry in medicine also came early. Industry has had much effect on usage of chemical names. Trade names are numerous and frequently different manufacturers of a given chemical compound apply different names to the product thus variously produced. These names sometimes appear in technical literature without adequate definition and are troublesome to the reader. Occasionally a trade name, as *adrenaline*, comes to be so commonly used that it is taken over into the native language as a regular word. If a trade-mark name has not reached such a stage, usage favours a capital letter to begin the name when written or printed.\* Good sources of information on trade names are: "Chemical Synonyms and Trade Names," by Gardner (The Technical Press, Ltd., London, 1936), "Trade-Names Index" (Special Libraries Assocn., New York, 1941); "Where to Find the New Trade Names," by Amoss (A. M. Amoss, Edgewood Arsenal, Maryland, 1940); "Modern Drug Encyclopædia and Therapeutic Guide," by Gutman (New Modern Drugs, New York City, 1941); "The Condensed Chemical Dictionary," by Gregory (Reinhold Publishing Corporation, New York City, 3rd ed., 1942); "Chambers's Technical Dictionary," by Tweney and Hughes (The Macmillan Company, New York and London, 1940); "The Merck Index" (Merck & Co. Inc., Rahway, N.J., 5th ed., 1940); "New and Non-official Remedies" (American Medical Association, Chicago, Illinois, appears annually); and (for dye names) "Colour Index," by Rowe (Society of Dyers and Colourists, Bradford, Yorkshire, England, and D. Van Nostrand Co., New York, 1924).

Industry tends to lag behind in the reform of chemical nomenclature, but there has been improvement in this respect in recent years.

**Spoken and Written Forms.**—Sometimes names which are satisfactory for use when written or printed are not completely satisfactory as spoken words because pronunciation is identical with that of some other name. The words "*benzene*" and "*benzine*" provide an example and so do "*fluorene*" and "*fluorine*." This situation often results from changes in endings to conform with nomenclature rules. Benzene was previously called *benzol*.

Conflicting usage is very common in the written form of organic names in that some authors use a single word without hyphens, as *phenyldiethylcarbinol*; some hyphenate, as *phenyl-diethyl-carbinol*; and others split such names into parts, as *phenyl diethyl carbinol*. It is considered good practice to limit the use of hyphens in organic names to the attachment of position numbers, symbols, and the like, as *1-sec-butyl-4-iodobenzene* and *ω-amino-m-toluic acid*. Some chemical names are properly single words whereas others are properly made up of two or more separate words. In an effort to help bring about better uniformity in practice in this respect and to provide other information useful in name construction, the following rules

were adopted by the American Chemical Society in 1931 (Proc. Amer. Chem. Soc. 1931, 40-41):

1. When a hydrogen atom of a compound is substituted by another atom or group, the name of this compound may be retained as the root of the name for the substituted compound. In such names, the prefix (denoting the substituent) is to be directly attached to the root and not spaced from it.

The position of monosubstituents is never labelled with compounds whose replaceable hydrogens are all equivalent, as methane, acetylene, benzene, hydrazine, carbinol, acetic acid, glyoxylic acid, acetone, and arsine. With compounds which contain more than one type of replaceable hydrogen, such as toluene, aniline, propionic acid, benzoic acid, hydroxylamine, acetophenone, and furan, ambiguity is avoided by labelling the position of substitution with numerals or with such labels as *ortho* or *o*-, *meta* or *m*-, *para* or *p*-, *alpha* or *α*-, *omega* or *ω*-.  
Examples:

diphenylmethane	and not	diphenyl methane
chlorobenzene	and not	chloro benzene
dimethylketen	and not	dimethyl keten
phenylhydrazine	and not	phenyl hydrazine
2-methyl-2-hexanol*	and not	2-methyl 2-hexanol
or		
methyl-2-hexanol-2	and not	methyl-2 hexanol-2
or		
2-methylhexanol-2	and not	2-methyl hexanol-2

\* Whether the numerals should be "fore" or "aft" or "fore and aft" is at present a debatable question.

1a. "*Amine*" is regarded as a contraction of "*ammonia*," and thus is used as the root to which the names of the substituents are directly attached as prefixes. This makes for uniformity with "*arsine*," "*aniline*," "*hydrazine*," etc., and distinguishes it from such names as *alcohol*, *ether*, or *ketone* which only represent types. Thus, *methylamine* is preferred to *methyl amine*, *ethylenediamine* to *ethylene diamine*, *triphenylarsine* to *triphenyl arsine*, *N,N*-dimethylaniline to *N,N*-dimethyl aniline and *p*-tolylhydrazine to *p*-tolyl hydrazine.

2. Since there is not a definite unsubstituted compound which is designated by *alcohol*, *ether*, or *ketone*, these terms are always used as separate words.

Examples:

ethyl alcohol  
*n*-butyl alcohol  
 dimethyl ether  
 methyl ethyl ether and not methylethyl ether  
 dimethyl ketone  
 methyl ethyl ketone and not methylethyl ketone  
*p*-bromophenyl *m*-tolyl ketone

3. If two words are used in naming aldehydes or nitriles, the first word is the same as the first word of the name of the corresponding acid. If, as is usually the case, one word is used for these names, the first word of the name of the acid is suitably altered to become a prefix. Usually, this alteration is a detachment of *ic* for aldehydes, as *acetaldehyde*, *propionaldehyde*, contractions of *acetic aldehyde* and *propionic aldehyde*, respectively. However, in naming *benzaldehyde*, *oic* has been detached. With *nitriles*, an *o* is usually introduced for euphony, as *acetonitrile* and *butyronitrile*, but the contraction may go back to an *o* as *propionitrile*.

\* In this Dictionary, italicised words in inverted commas may be registered trade names.—EDITOR.

4. *iso*Cyanate is a separate word. Thus,  $C_6H_5 \cdot NCO$  is phenyl *isocyanate*. This practice is correct for esters in general.

5. In naming metallo-organic compounds, the alkyl groups should precede and be directly attached to the name of the metal. Thus, methylmercuric iodide, diethylzinc, ethylmagnesium bromide, tetraethyllead, and tetramethylgermanium.

**Symbols and Abbreviations.**—Symbols for substances play an extremely important rôle in chemistry. The story of chemical symbols (*cf.* Hackh, *Evolution of chemical symbols*, J. Amer. Pharm. Assoc. 1918, 7, 1038-1042), which can only be suggested in barest outline here, constitutes a miniature history of this science.

Egyptian inscriptions show hieroglyphics for gold, silver, copper, iron, and lead. The alchemists used symbols to denote a good share of the substances which they knew. These were drawings, not letter symbols, and the same is true of the system of symbols worked out by Dalton, the originator of the atomic theory. His system was based on the circle as the conventional representation of the atom.

The chemists of the period of the antiplilogistic revolution were the first to invent signs founded on a reasonable principle the object of which was to indicate the compositions of substances. Their symbols were complicated, however.

The first real step towards making chemical symbols an international language of chemistry was taken by Berzelius (Thompson's *Annals of Philosophy*, 1813, 2, 443). His introduction of letter symbols and their use in the modern sense to denote proportions of elements in a compound constitute one of the great chemical contributions. Modern chemists still use his principle and most of his symbols.

Chemical literature contains, besides chemical formulas, many symbols and abbreviations the meaning of which is not always self-evident or familiar. Lack of general agreement on physical and physicochemical symbols has caused a certain amount of confusion, and has led to efforts at standardisation (*see* "Physical Chemistry," below). A comprehensive list of both symbols and abbreviations has been published as Appendix 2 in E. J. Crane and A. M. Patterson, "Guide to the Literature of Chemistry," Wiley & Sons, New York, 1927.

#### INORGANIC NOMENCLATURE.

While organic chemistry far outstrips inorganic chemistry in present-day active interest, as shown by the number of workers, published papers, and applications, the earlier chemists were primarily concerned with inorganic substances and the beginning of systematic nomenclature is really a chapter in inorganic chemistry. In 1770 Bergmann ("Meditationes de systemate fossilium naturali") proposed a new chemical nomenclature which has some suggestion of system, but to Guyton de Morveau (*J. physique*, 1782, 19, 310, 382; *Ann. Chim. Phys.* 1798, [i], 25, 205) belongs the credit of making the first attempt towards a convenient chemical nomenclature. Guyton de Morveau's beginning led to the publication in 1787 of "*Méthode de Nomenclature Chimique*," by de Morveau, Lavoisier,

Bertholet, and de Fourcroy, a landmark in the development of chemistry. These chemists may be regarded as forming the first chemical nomenclature committee, and they did their work so well that their general plan is still followed. They brought order out of chaos. Lavoisier writes of the need for reform, de Morveau explains the principles of the new nomenclature method, and de Fourcroy explains the extensive tabular listing of old and proposed new names.

de Morveau and Lavoisier were probably influenced by the then recently announced system of Linnæus for naming plants and animals. This involved the use of a generic and a specific name (two words) in place of the clumsy method of naming previously in use.

The principles were laid down that every substance is to be regarded as an element until proven to be otherwise and that the name of a compound is to exhibit the elements and as far as possible the relative proportions thereof. The new nomenclature was based principally on the combinations of oxygen with other elements. The product of the union of a simple substance, generally non-metallic, with oxygen was called an acid. The product of the union of a metallic substance with oxygen was called an oxide. A salt was the product of the union of an acid and an oxide. The union of a metallic substance with sulphur or phosphorus produced a sulphide or a phosphide, respectively. The acids or oxides were given names of which the generic part was the word "acid" or "oxide" and the specific part was an adjective derived from the other element in the compound. Thus, one of the products of the union of sulphur with oxygen was called sulphuric acid and a product of lead with oxygen was called lead oxide or plumbic oxide. The same principle supplied names for sulphides, phosphides, and, later, chlorides.

But some substances combine with oxygen to produce more than one acid or oxide. These were distinguished by an alteration of the termination of the specific name, or by the addition of a Greek prefix. Sulphur, for example, combines with oxygen to produce acids of various degrees of sulphur oxidation, which were designated by the terms sulphuric, sulphurous, or hyposulphurous acid; lead forms more than one oxide, indicated by the terms lead protoxide and lead dioxide.

In names adopted for salts the generic part was derived from the acid, and the specific from the metallic base. Thus, the product of the union of lead oxide with sulphuric acid was called lead sulphate or plumbic sulphate. To indicate the salts of acids with variously oxidised sulphur, the termination was varied. The salts of sulphuric acid were sulphates, those of sulphurous acid, sulphites; the salts of nitric acid were nitrates, those of nitrous acid, nitrites.

It will be noted that the use of significant endings in chemical nomenclature goes back as far as this first real systematisation. It will be noted also that long before the theory of electrolytic ionisation was introduced names were invented which have proved suitable for the designation of a positive and a negative part of a compound.

There was some early confusion in distin-

guishing between oxides (acid anhydrides) and acids and it is still the practice of some chemists to speak of such oxides as acids. It is not uncommon, for example, for carbon dioxide to be referred to as "carbonic acid" and for silica to be called "silicic acid."

In addition to his contribution of the modern type of chemical symbol, Berzelius, starting in 1811 (*J. physique*, 73, 258), did much to extend and amplify the nomenclature introduced by de Morveau and Lavoisier. He divided the elements into the metalloids and metals according to their electrochemical character and the positive oxygen compounds into suboxides, oxides, and peroxides. His corresponding division of the acids, designated according to degree of oxidation, has been little altered since. His method of designating the chlorine compounds corresponded to that for the oxides so that such names as subchloride, chloride, and perchloride resulted. Berzelius tried to apply the same principles in the naming of organic compounds, but not enough was known about them then for a rational nomenclature to be devised.

In 1834 Liebig advanced the idea of so-called "polybasic" acids and this led to further nomenclature developments.

**International Nomenclature Rules.**—As chemical knowledge increased and the number of known compounds multiplied and were named or spoken of by an increasing number of individuals it is only natural that discrepancies in practice should grow in number. In 1923 the Nomenclature Committee of the British Chemical Society and that of the American Chemical Society agreed on ten rules covering some of the more commonly disputed points. Some of these relate to endings which have a classification significance. These rules, which grew out of some directions to authors issued by the Journal of the Chemical Society follow:

1. In naming a compound so as to indicate that oxygen is replaced by sulphur the prefix *thio* and not *sulpho* should be used (sulpho denotes the group  $\text{SO}_3\text{H}$ ); thus,  $\text{HCNS}$ , thiocyanic acid;  $\text{H}_3\text{AsS}_4$ , thioarsenic acid;  $\text{Na}_2\text{S}_2\text{O}_3$ , sodium thiosulphate;  $\text{CS}(\text{NH}_2)_2$ , thiourea. The only use of *thio* as a name for sulphur replacing hydrogen is in cases in which the sulphur serves as a link in compounds not suitably named as mercapto derivatives; thus,  $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , thiobisanioline. *Hyposulphurous acid*, not hydrosulphurous acid, should be used to designate  $\text{H}_2\text{S}_2\text{O}_4$ .

2. The word *hydroxide* should be used for a compound with  $\text{OH}$  and *hydrate* for a compound with  $\text{H}_2\text{O}$ . Thus, barium hydroxide,  $\text{Ba}(\text{OH})_2$ ; chlorine hydrate,  $\text{Cl}_2\cdot 10\text{H}_2\text{O}$ .

3. Salts of chloroplatinic acid are *chloroplatinates* (not platinichlorides). Similarly salts of chloroauric acid are to be called *chloroaurates*.

4. Hydroxyl derivatives of hydrocarbons are to be given names ending in *-ol*, as glycerol, resorcinol, pinacol (not pinacone), mannitol (not mannite), pyrocatechol (not pyrocatechin).

5. The names of the groups  $\text{NH}_2$ ,  $\text{NHR}$ ,  $\text{NR}_2$ ,  $\text{NH}$ , or  $\text{NR}$  should end in *-ido* only when they are substituents in an acid group, otherwise

in *-ino*; thus,  $\text{MeC}(\text{:NH})\text{OEt}$ , ethyl imidoacetate;  $\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\beta$ -aminopropionic acid (not amidopropionic acid);

$\text{PhNH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,

$\beta$ -anilinopropionic acid;  $\text{CH}_3\text{C}(\text{:NH})\text{CO}_2\text{H}$ ,  $\alpha$ -iminopropionic acid.

6. Hydroxy-, not oxy-, should be used in designating the hydroxyl group; as *hydroxyacetic acid*,  $\text{HO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , not *oxyacetic acid*. *Keto-* is to be preferred to *oxy-* or *ozo-* to designate oxygen in the group  $-\text{CO}-$ .

7. The term *ether* is to be used in the usual modern acceptation only and not as an equivalent of *ester*.

8. Salts of organic bases with hydrochloric acid should be called *hydrochlorides* (not hydrochlorates nor chlorhydrates). Similarly hydrobromide and hydroiodide should be used.

9. German names ending in *-it* should be translated *-ite* rather than *-it*, as *permutite*. If it seems desirable to retain the original form of a trade name it should be placed in quotation marks, as "Permutit." Alcohols such as dulcitol (German Dulcitol) are exceptions.

10. German names of acids should generally be translated by substituting *-ic acid* for *"-säure"*. Some well-established names are exceptions, as *Zuckersäure* (saccharic acid), *Milchsäure* (lactic acid), *Valeriansäure* (valeric acid), etc. For a few well-established names it is correct to translate *"-insäure"* *-ic acid* instead of *-inic acid*. *E.g.*, *Acridinsäure* is acridic acid. Names ending in *"carbonsäure"* are to be translated *-carboxylic acid* (not *carbonic acid*).

These rules have been widely followed and are still to be recommended as a guide, although they cover the ground only partially and there has been some duplication of the points made in later rules issued by the International Union of Chemistry. It has seemed best to report these rules here as a unit even though they have a bearing on both organic and inorganic chemistry.

In view of the international aspect of chemical nomenclature it is but natural that one of the objectives of the International Union of Chemistry (originally called the International Union of Pure and Applied Chemistry) should be nomenclature standardisation and that it should appoint commissions and working committees on nomenclature soon after its organisation in 1919. Separate commissions were appointed for inorganic chemistry, organic chemistry, and biological chemistry. Following earlier French and German committee reports, the first report of the Committee for the Reform of Inorganic Chemical Nomenclature was written in 1926 by Marcel Delépine and issued as a separate by the International Union. This was later published in *Bull. Soc. chim.* 1928, [iv], 43, 289 and elsewhere. There have been several reports as the work of the committee has progressed under W. P. Jorissen as chairman, but it was not until 1940 that a matured and widely accepted report appeared (*Ber.* 1940, 73 [A], 53-70; *J.C.S.* 1940, 1404-1415; *J. Amer. Chem. Soc.* 1941, 63, 889-897). History will hardly record the year 1940 as one of general progress in international co-operation; nevertheless this 1940 report, a culmination of work

done, and in part reported, during the last two decades, is an outstanding accomplishment for improved and internationally standardised inorganic nomenclature.

Much credit in the development of these rules is due to H. Rémy, whose recommendations were published as a 64-page separate, and R. J. Meyer, whose report appears in *Chem. Weekblad*, 1936, 33, 722-729 and in *Helv. Chim. Acta*, 1937, 20, 159-175. In view of its importance and of its practical usefulness in present-day chemical communication, the report, with some abbreviation and paraphrasing, and with occasional comment in brackets by the authors of this article, is reproduced here as the most satisfactory way to survey approved usage.

### I.U.C. RULES FOR NAMING INORGANIC COMPOUNDS.

The aim of the Rules is the unification of inorganic chemical nomenclature and the removal of names which are out of date or incorrect.

#### A. General.

**Names and Formulae.**—A chemical compound can be designated in two ways: (1) by means of the formula, (2) by means of the name.

(1) Formulae should be widely used in designating inorganic compounds since they provide the simplest and clearest method of doing this. Their significance is, moreover, the same in all languages and for brevity and saving of space they are unequalled.

Formulae are of particular use when dealing with complicated compounds. Their use must naturally be avoided in cases where any uncertainty might be introduced.

(2) When giving names to compounds there are two possibilities: (a) systematic names, (b) trivial names.

(a) In the case of systematic names it is not always necessary to indicate stoichiometric proportions in the names, because a glance at the formula shows at once the quantitative and atomic composition.

In many cases sufficient abbreviation of the systematic name can be secured by omitting all numbers, indications of valency, etc., which are not needed in the given circumstances. For instance, indication of the valency or atomic proportions is generally not required with compounds of elements of essentially constant valency.

**Examples:** Aluminium sulphate instead of aluminium(III) sulphate; potassium chloroplatinate instead of potassium hexachloroplatinate(IV); potassium cyanoferrate(II) instead of potassium hexacyanoferrate(II); potassium cyanoferrate(III) instead of potassium hexacyanoferrate(III) (see p. 603a).

(b) Distinction must be made between: (aa) pure trivial names, (bb) incorrectly formed names.

(aa) Pure trivial names are those which are free from false scientific significance or other wrong indications. Examples are saltpetre, caustic soda, quicklime. The use of such pure trivial names is permissible.

(bb) Incorrectly formed names are those which were originally constructed to bring out certain ideas on the composition or constitution of the compounds in question, but which are now contrary to present views and knowledge. Such names are sulphate of magnesia, carbonate of lime, nitrate of potash, acetate of alumina. Their use is widespread, but scientifically they are incorrect.

Such names should not be used in any circumstances.

#### B. Binary Compounds.

**1. Position of Constituents in Names and Formulae.**—The electropositive constituent should always be put first in the formula and in the name whenever it is recognisable from the character of the compound—as in salts or salt-like compounds. The name of the electronegative constituent is given the termination *-ide*. In the case of nonpolar compounds and of those in which it is not known which constituent in the compound is to be regarded as electropositive, that constituent should be placed first which has the more electropositive character in the free condition.

**Examples:** Sodium chloride, silver sulphide, lithium hydride, boron carbide, oxygen difluoride.

The above rule summarises the customary usage in English and German. Exactly the opposite applies in French and Italian so that in these languages the order of constituents in formulae will also be just the opposite to that which is correct in English and German. Such differences are due to the very nature of the several languages and cannot be eliminated. Names are also in use in some languages, particularly German, which are obtained by simple juxtaposition of the separate names of the constituents without any termination.

**Example:** Chlorwasserstoff.

#### II. Indication of the Proportions of Constituents.

There are two possible ways of indicating the proportions of the constituents in chemical compounds. It can be done: (1) by indicating the valency, (2) by giving the stoichiometric composition, or the functional nature.

(1) Indication of the electrochemical valency in the names of compounds should be made only by Stock's method. This is done by means of Roman figures, placed in parentheses and following, without hyphen, immediately after the names of the elements to which they refer.

**Examples:** CuCl Copper(I) chloride.  
CuCl<sub>2</sub> Copper(II) chloride.  
FeO Iron(II) oxide.  
Fe<sub>2</sub>O<sub>3</sub> Iron(III) oxide.

The system of valency indication by terminations such as *-ous*, *-ic* (ferrous, ferric) which was previously in use has proved unsatisfactory and should now be avoided not only in scientific but also in technical writing. [It is not likely that chemists will give up entirely the use of *-ous* and *-ic* endings for such compounds and it seems suitable to regard some of these rules as alternatives so long as the older nomenclature is completely clear. For example, cuprous chloride and cupric chloride for CuCl and CuCl<sub>2</sub>, respectively, are likely to be retained in general usage, but the Stock method should, and probably will, come into use in dealing with compounds involving more than two valency stages of one element, such as the halides of vanadium, molybdenum, and tungsten, for the *-ous* and *-ic* endings are then inadequate and lack significance, even when additional valency stages are represented in other ways as by terms like *metavanadic*, *ferroferriic*, *hypovanadous*, and *permanganous*.] If the valency needs to be shown in formulae or when using symbols for the elements, then the Roman figures should be placed just above the appropriate symbols on the right-hand side.

**Examples:** Cu<sup>I</sup> salts.  
Fe<sup>II</sup> compounds.

(2) Indication of the stoichiometric composition should be made by means of Greek numerical prefixes which should precede, without hyphen, the constituent to which they refer. This method of showing the composition in names instead of by means of the valency is customary more especially with nonpolar compounds. It is also indicated in cases where the composition differs from that to be expected from the usual valency or in those in which the electrochemical valency is unknown. The prefix "mono" can generally be omitted; 8 should be indicated by "octa," 9 by "ennea." Greek prefixes above 12 are replaced by Arabic figures (without hyphen) as they are more easily understood. Arabic figures are also used for indicating fractions of molecules, although  $\frac{1}{2}$  can also be expressed by "heml." The functional system of naming compounds can be employed instead of the stoichiometric. This is used more particularly in French.

#### Examples:

	Stoichiometric system.	Functional system.
N <sub>2</sub> O	Dinitrogen (mon)oxide.	
NO	Nitrogen oxide.	
N <sub>2</sub> O <sub>3</sub>	Dinitrogen trioxide.	Nitrous anhydride.
NO <sub>2</sub>	Nitrogen dioxide.	
N <sub>2</sub> O <sub>4</sub>	Dinitrogen tetroxide.	
N <sub>2</sub> O <sub>5</sub>	Dinitrogen pentoxide.	Nitric anhydride.
As <sub>2</sub> F <sub>6</sub>	Disilver fluoride.	
Fe(CO) <sub>5</sub>	Iron tetracarbonyl.	
FeS <sub>2</sub>	Iron disulphide.	

The formula is to be preferred to an awkward name, thus Na<sub>12</sub>Hg<sub>13</sub>, not 12 sodium 13 mercuride.



Out of date and superfluous terms such as Oxydul, Sulfur, Cyanur, Chlorur, etc., for compounds of lower valency stages, should vanish from the German language, both because they lack precision and because of the way in which many of these terms are used in French.

**III. Designation of Intermetallic Compounds.**—Intermetallic compounds do not follow the usual laws of constant composition and must often be regarded rather as phases having a range of existence over which they are more or less homogeneous. There is lacking, at present, a clear understanding, and grouping together, of the laws which govern this class of compounds, so that any attempt at a rigid system of nomenclature would be premature.

For this reason the use of names for intermetallic compounds should be avoided and formulæ alone should be used in all cases; these formulæ should give the exact numbers of atoms if possible. A simplified formula which represents the compound in a satisfactory manner can be used in those cases where either the exact number of atoms cannot be stated or where an intermetallic compound has a wide range of composition. To avoid any danger of confusion with a compound of definite composition, a bar should be placed over the formula to show that the composition is variable.

*Example:* AuZn occurs as  $\beta$ -phase in the system Au-Zn as an intermetallic compound with properties which differ from those of the components Au and Zn. It is homogeneous over the range of 41–58 atom % Zn, so that all formulæ  $Au_{59}Zn_{41}$  to  $Au_{44}Zn_{56}$  would be correct. The shortened form  $AuZn$  or  $\overline{AuZn}$  may be used.

Compounds such as  $\overline{AuZn}$  which do not have a constant composition should be called "non-Daltonian" compounds to distinguish them from "Daltonian" compounds of constant composition.

**IV. Indicating the Mass, Atomic Number, and State of Ionisation on the Atomic Symbols.**—When dealing with nuclear reactions, the ordinary representation of an element by the plain symbol is not sufficient. The latter must be expanded so as to show the atomic mass and atomic number.

An index on the right and below the symbol is already used to show the stoichiometric proportion, while another on the right above the symbol shows the state of ionisation. The corresponding positions on the left are available for the atomic number and mass. We then have:

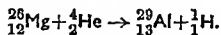
right lower index . . .	the number of atoms
right upper index . . .	the state of ionisation
left lower index . . .	the atomic number
left upper index . . .	the mass

*Example:*



This represents a singly ionised chlorine *molecule*  $\text{Cl}_2$ , each atom of which has the atomic number 17 and mass 35.

The following is an example of an equation for a nuclear reaction:



[Chemists and physicists in America have established the custom of placing the atomic weight in the upper right-hand corner. Physicists naturally feel less bound by rulings of the International Union of Chemistry than do chemists. Physicists do much of the work involving such symbols and thus far they have not consented to change. This leaves American chemists confronted with the dilemma of breaking away from the practice of their colleagues in physics or of failing to observe this international ruling.]

**V. Group Names.**—Compounds of the halogens are to be called *halogenides* (not haloids nor halides), while the elements oxygen, sulphur, selenium, and tellurium may be called *chalcogens* and their compounds *chalcogenides*. [This choice of halogenides over halides is somewhat unpopular, as the shorter word is well established and seems unobjectionable.\*]

The alkali metals should not be called "alkalies" or the alkaline earth metals "alkaline earths," since these names are old-fashioned terms for the oxides of these metals and should be avoided in scientific language. If compounds are concerned, the use of

\* In the English nomenclature the use of the term *halogenides* is not enforced, and the term *chalcogenides* is not used.

"alkali" or "alkaline earth" as an abbreviation for "alkali metal" or "alkaline earth metal" is general and permissible, e.g., alkali chlorides.

In German "Kohlen-" is permissible as an abbreviation for "Kohlenstoff" in many carbon compounds.

#### C. Ternary Compounds, Quaternary Compounds, etc.

The preceding rules which have been developed for binary compounds are valid, when suitably extended, also for compounds of more than two elements.

Radicals having special names are treated like the elementary constituents of a compound when constructing names.

<i>Examples:</i> $\text{NH}_4\text{Cl}$	Ammonium chloride.
$\text{KCN}$	Potassium cyanide.
$\text{Fe}(\text{SCN})_3$	Iron(III) thiocyanate.
$\text{Pb}(\text{N}_3)_2$	Lead azide.

If several electropositive constituents are combined with one electronegative, then the rule holds that the most electropositive constituent is to be placed first, just as in the case of binary compounds. Similarly if a compound contains several electronegative constituents these should be placed, both in the name and in the formula, in order of increasing electronegative character so far as this is possible. [The use of an alphabetic order instead of the order of increasing electronegativity for compounds containing several electronegative constituents is sometimes preferred, on account of its simplicity.]

Sulphur replacing oxygen in an acid radical should always be indicated by "thio" (see under D), so that compounds of the radical SCN should be called "thiocyanates" not sulphocyanates and not sulpho- or thio-cyanides.

Names such as the following are permissible for mixed salts: lead chlorofluoride, lead sulphochloride. [Instead of names like lead chlorofluoride (for  $\text{PbClF}$ ), names of the type "lead chloride fluoride" are sometimes preferred.]

The terms aluminio-, boro-, beryllo-, etc., silicates should only be applied to silicates which contain Al, B, Be, etc., replacing part of the Si.

*Examples:*

Orthoclase,  $\text{K}[\text{AlSi}_3\text{O}_8]$ , is an aluminosilicate (potassium aluminotrisilicate).

Spodumene,  $\text{LiAl}[\text{Si}_2\text{O}_6]$ , is an aluminium silicate (lithium aluminium disilicate).

Muscovite,  $\text{KA}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ , is an aluminium aluminosilicate.

#### D. Oxygen Acids.

Well-established names for the majority of the important simple oxygen acids have been in use for a long time, and their alteration is neither desirable nor necessary. It is only necessary to consider a number of cases in which uncertainty or confusion has arisen in the course of time owing to the employment of some names which are incorrect.

In the following tables are shown the names which should be used for the more important acids of sulphur, nitrogen, phosphorus, and boron as well as their salts.

Formula.	Acid.	Salt.
Acids and Salts of Sulphur.		
$\text{H}_2\text{SO}_2$	Sulphoxylic acid.	Sulphoxylate.
$\text{H}_2\text{S}_2\text{O}_4$	Dithionous acid.	Dithionite.
$\text{H}_2\text{SO}_3$	Sulphurous acid.	Sulphite.
$\text{H}_2\text{S}_2\text{O}_2$	Thiosulphurous acid.	Thiosulphite.
$\text{H}_2\text{S}_2\text{O}_5$	Pyrosulphurous acid.	Pyrosulphite.
$\text{H}_2\text{SO}_4$	Sulphuric acid.	Sulphate.
$\text{H}_2\text{S}_2\text{O}_3$	Thiosulphuric acid.	Thiosulphate.
$\text{H}_2\text{S}_2\text{O}_7$	Pyrosulphuric acid.	Pyrosulphate.
$\text{H}_2\text{SO}_5$	Peroxy(mono)sulphuric acid.	Peroxy(mono)sulphate.
$\text{H}_2\text{S}_2\text{O}_6$	Dithionic acid.	Dithionate.
$\text{H}_2\text{S}_x\text{O}_6$ ( $x=3, 4$ , etc.)	Polythionic acids.	Polythionates.
$\text{H}_2\text{S}_2\text{O}_8$	Peroxydisulphuric acid.	Peroxydisulphate.
Acids and Salts of Nitrogen.		
$\text{H}_2\text{N}_2\text{O}_2$	Hyponitrous acid.	Hyponitrite.
$\text{H}_2\text{NO}_2$	Nitroxyl acid.	Nitroxylate.
$\text{HNO}_2$	Nitrous acid.	Nitrite.
$\text{HNO}_3$	Nitric acid.	Nitrate.
$\text{HNO}_4$	Peroxyntitric acid.	Peroxyntitrate.



Formula.	Acid.	Salt.
Acids and Salts of Phosphorus.		
$H_3PO_2$	Hypophosphorous acid.	Hypophosphite.
$H_3PO_3$	Phosphorous acid.	Phosphite.
$H_4P_2O_5$	Pyrophosphorous acid.	Pyrophosphite.
$H_4P_2O_6$	Hypophosphoric acid.	Hypophosphate.
$H_3PO_4$	(Ortho)phosphoric acid.	(Ortho)phosphate.
$H_4P_2O_7$	Pyrophosphoric acid.	Pyrophosphate.
$HPO_3$	Metaphosphoric acid.	Metaphosphate.
$H_3PO_5$	Peroxy(mono)phosphoric acid.	Peroxy(mono)phosphate.
$H_4P_2O_8$	Peroxydiphosphoric acid.	Peroxydiphosphate.

## Acids and Salts of Boron.

$H_3BO_2$	Boronic acid.	—
$H_2B_2O_4$	Hypoboric acid.	Hypoborate.
$H_3BO_3$	Orthoboric acid.	Orthoborate.
$HBO_2$	Metaboric acid.	Metaborate.
$H_2B_4O_7$	Tetraboric acid.	Tetraborate.

For other polyboric acids, see under F. II. [Decisions made on the six following points arising out of the above tables are explained in some detail in the report. The notes to 3 and 5 are of special interest.]

1.  $H_2S_2O_4$  Dithionous acid, and not *hydrosulphurous* or *hyposulphurous* acid; salts are dithionites.
2.  $H_2S_2O_3$  Thiosulphuric acid, and not *hyposulphurous* acid; salts are thiosulphates.
3.  $H_2SO_5$  Peroxymonosulphuric acid, and not *persulphuric* acid.
4.  $H_2NO_2$  Nitroxyl acid, and not *hydronitrous* acid, salts are nitroxylates.
5.  $H_2B_4O_7$  Tetraboric acid, and not *pyroboric* acid; salts are tetraborates.
6.  $H_2PO_3$  Salts to be called hypophosphites.

[Some are delaying in the adoption of "dithionous acid" for  $H_2S_2O_4$  since there is some doubt as to whether this compound is symmetrical.]

Note to 3: A distinction must be made between those acids or salts which are derived by substitution from hydrogen peroxide and in consequence contain peroxidic oxygen  $-O-O-$  and those which are derived from the highest oxidation stages of some elements and are free from peroxidic oxygen. The last-named are correctly called *per* salts (such as  $NaClO_4$ ,  $KMnO_4$ ).

The first group, such as  $R_2S_2O_4$  and  $R_3PO_5$ , must be separated from the genuine *per* salts and called *peroxy* salts, the corresponding acids being *peroxy* acids.

Examples:  $H_2SO_5$  Peroxymonosulphuric acid.  
 $H_4P_2O_8$  Peroxydiphosphoric acid.  
 $NH_4BO_3$  Ammonium peroxyborate.

In the same way the oxides derived from  $H_2O_2$  should be called *peroxides*, and not *superoxides* or *hyperoxides*.  
 Note to 5: The prefixes "ortho," "meta," and "pyro" are used generally in the sense that the term "ortho" is applied to the most hydroxylated acid known either in the free state or as salts or esters.

Examples:  $H_3BO_3$  Orthoboric acid.  
 $H_4CO_4$  Orthocarbonic acid.  
 $H_4SiO_4$  Orthosilic acid.  
 $H_3PO_4$  Orthophosphoric acid.  
 $H_6TeO_6$  Orthotelluric acid.  
 $H_2SiO_6$  Orthosilicic acid.

The pyro and meta acids are derived from the ortho acids by removal of water in stages. Pyro acids are those which have lost 1 molecule of  $H_2O$  from 2 molecules of ortho acid. (Examples:  $H_2S_2O_7$ ,  $H_2S_2O_8$ ,  $H_4P_2O_7$ ,  $H_4P_2O_8$ .) This rule does not apply, however, to the polyboric acid  $H_2B_4O_7$  ( $=2B_2O_3 \cdot H_2O$ ) which contains less water than metaboric acid,  $HBO_2$  ( $=B_2O_3 \cdot H_2O$ ). To avoid breaking the rule the acid  $H_2B_4O_7$  should not be called "pyroboric acid," but "tetraboric acid" in agreement with the proposals for the naming of isopoly acids (see F. II).

Replacement of O by S.—Acids which are derived from oxygen acids by replacement of O atoms by S atoms are to be called *thio* acids, their salts *thio* salts.

Examples:  $H_2CS_3$  Trithiocarbonic acid.  
 $Na_3SbS_4$  Trisodium tetrathioantimonate (sodium thioantimonate for short).

The group  $[H_3O]^+$ .—When the hydrogen ion is considered to occur (in aqueous solution or in a compound) in the form  $[H_3O]^+$ , it is advisable to call it the *hydronium* ion (not *hydroxonium* ion).

## E. Salts.

I. General.—Salts should always be named so that the name of the metal or electropositive radical precedes that of the acid radical which carries the termination -ate, -ite, or -ide.

Examples: Silver nitrate, magnesium sulphate, calcium carbonate, sodium nitrite, iron sulphide, potassium cyanide.

Names such as "nitrate of silver," "sulphate of magnesium" are permissible, but the use of the name of the metal oxide in place of that of the metal, e.g. "sulphate of magnesia," "carbonate of lime," etc., is definitely wrong, and should not be employed (see A.).

In the case of mixed or double salts the rules given under C should be applied.

Examples:  $KN_3CO_3$  Potassium sodium carbonate.  
 $KCaPO_4$  Potassium calcium phosphate.  
 $NH_4MgPO_4$  Ammonium magnesium phosphate.

Salts of nitrogen compounds. If regarded as coordination compounds like ammonium chloride,  $NH_4Cl$ , are to be designated as "-onium" or "-inium" compounds.

Examples: Tetramethylammonium chloride, hydrazinium chloride, pyridinium chloride.

If, however, the nitrogen compounds are regarded as addition compounds, then the rules derived for these will apply (see F. V).

II. Acid Salts (Hydrogen Salts).—The rational names for acid salts are formed by using "hydrogen" for the hydrogen atoms which they contain. The hydrogen is to be named last of the electropositive constituents.

Examples:  $KHSO_4$  Potassium hydrogen sulphate.  
 $NaHCO_3$  Sodium hydrogen carbonate.  
 $Na_2HPO_4$  Disodium hydrogen phosphate.  
 $NaH_2PO_4$  Sodium dihydrogen phosphate.

In complicated cases use formulae.

Examples:  $4K_2SO_4 \cdot 3H_2SO_4 \rightarrow K_9H_6(SO_4)_7$  rationally: Octapotassium hexahydrogen heptasulphate.  
 $5K_2SO_4 \cdot 3H_2SO_4 \rightarrow K_9H_3(SO_4)_8$  rationally: Pentapotassium trihydrogen tetrasulphate.

If it is desired to emphasise the type of compound rather than its composition, the term *acid salts* (monoacid, diacid, etc.) can be used as well as such expressions as primary, secondary, tertiary salts. Designation in terms of the acid: base ratio by means of "bi" is not in agreement with the fundamental principles of rational nomenclature. It is therefore wrong to say "bicarbonate," "bisulphate," "bisulphite."

III. Basic Salts.—Basic salts which can be shown to contain hydroxyl groups and which can be considered and named as addition compounds of hydroxides to neutral salts are called *hydroxy* salts.

Example:  $Cd(OH)Cl$  Cadmium hydroxychloride.

When the hydroxy group is bound in a complex compound Werner's system of notation should be used, according to which the hydroxyl groups are designated *hydroxo* or *ol* groups. Basic salts in which there are oxygen atoms as well as acid radicals attached to the metal are called *oxy* salts. If they contain radicals with special designations, names derived from these can be employed.

Examples:  $BiOCl$  Bismuth oxychloride or bismuthyl chloride.  
 $UO_2(NO_3)_2$  Uranium(VI) dioxynitrate or uranyl nitrate.

## Examples:

$[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$	Hexa-aquoehromium(III) chloride.
$[\text{Cr}_3\text{Ac}_6(\text{OH})_2]\text{X}$	Hexa-acetatodihydroxotrichromium(III) salt.

In designating complex anions of acids or salts the valency of the central atom is given in parentheses after the name of the complex which ends in -ate. The Latin names of metals must often be used in this connection for reasons of euphony.

## Examples:

$\text{H}_2[\text{P}(\text{Cl})_4]$	Hydrogen hexachlorophosphate(IV)
$\text{H}_4[\text{Fe}(\text{CN})_6]$	Hydrogen hexacyanoferrate(II)
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
$\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitrocobaltate(III)
$\text{K}[\text{Au}(\text{OH})_4]$	Potassium tetrahydroxoaurate(III)

For neutral complexes (non-electrolytes) it is not necessary to give the valency of the central atom. If it is desired to emphasise the valency, this can be done as with the complex cations. Indication of the valency is not necessary when the number of the ionised atoms or groups is given in the name.

## Examples:

$[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$	Hexa-aquoehromium trichloride.
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Tetrapotassium hexacyanoferrate.
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Tripotassium hexacyanoferrate.

This method of naming is, however, only to be recommended in those cases where the electrochemical valency of the central atom is doubtful, as for instance with compounds containing NO in the complex. [At this point one is likely to wonder about the -ite and -ate endings versus the invariable -ate ending with a Roman numeral. It seems satisfactory to use such well-established names as chloroplatinate where there is no ambiguity, but perhaps the tendency should be in the direction of the use of the invariable -ate ending where there is any question. Even with simple oxygen acids Chemical Abstracts uses the invariable -ate where confusion exists in -ite and -ate names (notably with the ferrites and ferrates). For the complex acids Chemical Abstracts prefers an -le ending with a Roman numeral, as chloroplatinic(IV) acid (in this case the numeral could be dropped), to "hydrogen -ate" names, as hydrogen hexachloroplatinate(IV). The German version of the rules uses the name Hexachloroplatin(IV)-säure.]

**Order of the attached atoms or groups.**—Atoms or groups co-ordinated in the complex are to be mentioned in the name in the order (I) *acidic groups* such as chloro (Cl), cyano (CN), cyanato (NCO), thiocyanato (NCS), sulphato (SO<sub>4</sub>), nitro (NO<sub>2</sub>), nitrito (ONO), oxalato (C<sub>2</sub>O<sub>4</sub>), and hydroxo (OH); (II) *neutral groups*: aquo (H<sub>2</sub>O), substituted amines [C<sub>2</sub>H<sub>5</sub>(NH<sub>2</sub>)<sub>2</sub>-en] and last of all ammine (NH<sub>3</sub>).

**II. Isopoly Acids and their Salts.**—As isopoly acids in the widest sense are to be understood those acids which can be regarded as resulting from two or more molecules of one and the same acid by elimination of water. In this sense the pyro and meta acids which are formed from ortho acids by removal of water are also to be included among the isopoly acids.

Even though the rule holds for the poly acids in an accentuated form that formulae should be used for characterising compounds in complicated cases, there is yet need for a rational nomenclature if only for designating the groups of compounds. There belong to the isopoly acids as especially important representatives the borie, silicic, molybdic, tungstic, and vanadic acids. Rules will be considered with reference to them, therefore.

It is proposed that the empirical formulae should always be resolved into the base anhydride:acid anhydride ratios. For this it is unnecessary to go into the still obscure and unsettled questions of the constitution of these compounds, and this avoids introducing into the method of designation any essential factor that might have to be changed in consequence of an eventual change in conception of the constitution.

This procedure gives a method of representation for this class of compounds which is clear and straightforward and very suitable for systematic treatment. Characterisation by means of the base anhydride:acid anhydride ratio has already thoroughly justified itself in the systematic description of the poly acids and their salts in Gmelin's "Handbuch der anorganischen Chemie." It has always made possible a classification which was free from contradictions.

The following equally satisfactory methods for constructing names are available:

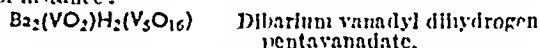
1. The composition, referred to the simplest empirical formula, is given by means of Greek numerical prefixes just as with other compounds (cf. B. II).

2. The simplest formula which expresses the analytical results for the compound in terms of base anhydride and acid anhydride is resolved into these. The ratio base anhydride:acid anhydride is shown in the name by means of Arabic figures in parentheses.

In both cases the basic component is to be named before the acid. Acid hydrogen atoms are to be indicated by "hydrogen" and should always be given (also in the names of the free acids).

These proposals have been carried out for a number of borates, silicates, molybdates, tungstates, and vanadates, as shown in the tables opposite.

In more complicated cases the formula itself is best employed. Even though a correct systematic name is possible in such cases, it is generally unwieldy, as, for instance:



In a similar way, for example, the compounds of the tungstic acids with organic bases are grouped together as "tungstates of organic bases." Subordinated to this group are the subgroups "methylammonium tungstates," "propylammonium tungstates," and so on, of which the individual compounds then follow with their formulae only, since an attempt to form names for each compound would lead to a cumbersome representation of their composition.

**III. Heteropoly Acids and their Salts.**—The formulae of the heteropoly acids and their salts are resolved into their constituent base and acid anhydrides as in the case of the isopoly acids, and for this purpose the simplest formula which expresses the analytic composition is employed.

This resolution is made for the acid into: Non-metallic acid, oxide of the acid-forming metal, water; for the salt into: salt of the nonmetallic acid (resolved perhaps into base anhydride:acid anhydride ratio), oxide of the acid-forming metal, water.

The numbers of atoms of the two acid-forming elements derived from the simplest formula are shown in the name by means of Arabic figures or Greek numerical prefixes. As a rule, names are used here only for the collective designation of groups of compounds. For individual compounds formulae are used for the most part.

## Examples:

$\text{R}_3\text{PO}_4 \cdot 12\text{MoO}_3$	Dodecamolybdophosphate
or $3\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{MoO}_3$	24-Molybdo-2-phosphate.
$\text{R}_3\text{PO}_4 \cdot 12\text{WO}_3$	Dodecatungstophosphate
or $3\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3$	24-Tungsto-2-phosphate.
$2\text{R}_2\text{PO}_4 \cdot 17\text{WO}_3$	17-Tungstodiphosphate
or $5\text{R}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17\text{WO}_3$	17-Tungsto-2-phosphate.
$\text{R}_6\text{B}_4\text{O}_{12} \cdot 12\text{WO}_3$	Dodecatungstoborate
or $5\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 24\text{WO}_3$	24-Tungsto-2-borate.
$\text{R}_4\text{SiO}_6 \cdot 12\text{WO}_3$	Dodecatungstosilicate
or $4\text{R}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3$	12-Tungstosilicate.

[Because they are so well established it seems likely that the following exceptions to the rules for naming complex compounds will continue to be encountered frequently in chemical literature: cobaltcyanide acid, cobaltcyanide, cobalthitrite, cobaltcyanide, cobalt-nitrite, ferricyanide acid, ferricyanide, ferrocyanide, phosphomolybdic acid, phosphotungstic acid, silicomolybdic acid, silicotungstic acid.]

**IV. Double Salts.**—The name of the double salt is formed by putting together the names of the simple salts from which it is formed. The order of the cationic constituents should be that of decreasing electropositive character. Constituents common to both salts should be mentioned only once.

## Examples:

$\text{KCl} \cdot \text{MgCl}_2$	Potassium magnesium chloride.
$\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$	Sodium calcium sulphate.
$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$	Calcium chloroaluminate. <sup>†</sup>
$\text{KCl} \cdot \text{MgSO}_4$	Potassium chloride magnesium sulphate.

\* If by so doing simpler numerical relations can be obtained.

<sup>†</sup> The German version has "Calciumchloridalumminat" (cf. Ber. 1910, 73 [A], 69).

In the third example only the group name is given, under which all the single members are collected. [It may sometimes be found difficult or impossible to know whether a double salt or a salt with a complex anion is under consideration. For example,  $3\text{NaF}\cdot\text{AlF}_3$  may be named sodium aluminium fluoride, or sodium fluoaluminate ( $\text{Na}_3\text{AlF}_6$ ), or it may be spoken of merely as a compound of sodium fluoride with aluminium fluoride.]

V. Hydrates, Ammoniates and other Addition Compounds.—The collective names *hydrate*, *peroxyhydrate* (not perhydrate), and *ammoniate* should be applied to compounds which contain molecules of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{NH}_3$ , respectively.

Either Greek numerical prefixes or Arabic figures can be used to show the number of such molecules present.

*Examples :*

$\text{CaCl}_2\cdot 6\text{H}_2\text{O}$	Calcium chloride hexahydrate or calcium chloride 6-hydrate.
$\text{CaCl}_2\cdot 4\text{H}_2\text{O}$	Calcium chloride tetrahydrate or calcium chloride 4-hydrate.
$\text{NaOOH}\cdot\text{H}_2\text{O}_2$	Sodium hydrogen peroxide peroxyhydrate.
$\text{AlCl}_3\cdot x\text{NH}_3$	Aluminium chloride ammoniate.

If it needs to be shown that the molecule in question forms part of a *complex*, then the compounds are to be named as *aquo* compounds, *peroxyhydrato* compounds, and *ammines* (cf. F. I.).

*Examples :*

$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$	Hexamminechromium(III) chloride.
$[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$	Hexa-aquochromium(III) chloride.
$[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$	Dichlorotetra-aquochromium(III) chloride dihydrate.

*Other addition compounds.*—Addition compounds containing added  $\text{PCl}_3$ ,  $\text{NOCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{C}_2\text{H}_5\text{-OH}$ , etc., are better shown by the formula than by a special name. For systematic consideration of this field it is advisable to make use of a group name.

*Examples :*

$\text{AlCl}_3\cdot 4\text{C}_2\text{H}_5\text{-OH}$	Compound of aluminium chloride with alcohol.
$\text{AlCl}_3\cdot \text{NOCl}$	Compound of aluminium chloride with nitrosyl chloride.
$\text{AlCl}_3\cdot \text{H}_2\text{S}$	Compound of aluminium chloride with hydrogen sulphide.

Group names: "Compounds of aluminium chloride with organic compounds," "with sulphur compounds," etc.

**Further Reform.**—In spite of the considerable effort which has been made to standardise inorganic chemical nomenclature there is still much room for improvement. Under the heading "The Need for Reform in Inorganic Chemical Nomenclature," Janet D. Scott (Chem. Reviews, 1943, 32, 73–97) has discussed the needs thoroughly. Her comprehensive paper is a good source of information as to the variety of usages, bad as well as good, which are encountered in chemical literature. It includes a bibliography of 70 references.

## ORGANIC NOMENCLATURE.

**Early Developments.**—Methods of naming carbon compounds have evolved with the progress of organic chemistry, as is well illustrated by the names given to the compound  $\text{C}_2\text{H}_5\text{-OH}$ . Following the fanciful names of the alchemists, of which "aqua vitæ" is the best known, came "spirit of wine" and *alcohol*; the latter term, originally meaning a fine powder, was perhaps transferred to the liquid because of the resemblance between sublimation and distillation. With the discovery of other similar compounds and the rise of the radical theory "alcohol"

became a class name and  $\text{C}_2\text{H}_5\text{-OH}$  was called specifically *ethyl alcohol* (at first with the dualistic formula  $\text{C}_2\text{H}_4\cdot\text{H}_2\text{O}$  or  $\text{C}_4\text{H}_{10}\text{O}\cdot\text{H}_2\text{O}$ ). Still later the Geneva name *ethanol* incorporated the compound into a comprehensive system of hydrocarbons, alcohols, acids, and other classes.

In the absence of a knowledge of structure compounds receive unsystematic or "trivial" names (see "General Influences," p. 594d). We know by such names a great number of organic compounds extracted from plant and animal materials. Many such substances are conveniently named from the plant, animal, or animal part in which they are found.

If a compound is known to contain one of several functional groups this additional fact can be indicated by an appropriate ending. The acid function was the first to be recognised in organic compounds; hence, such names as "acetic acid" (literally "vinegar acid," German *Essigsäure*) were coined long before the constitution of the acids was deciphered. These names of common acids have proved so convenient that they are still used in preference to the systematic structural names even when the latter are not longer. The basic function was also early recognised and came to be indicated by the suffix *-ine* (in German, *-in*). Thus we have many names of alkaloids, as *morphine* and *strychnine* (the spellings *morphia*, *strychnia*, etc., are now obsolete in chemical usage) and of other bases, as *aniline* and *pyridine*.

As other suffixes denoting function developed (e.g., *-ol* for alcohols and phenols, *-ene* for unsaturated hydrocarbons, *-one* for ketones) they were used in the same way. It is true that such terminations have not always been consistent (e.g., glycerine is not a base and pyrrol is not an alcohol or phenol); nevertheless, most of the exceptions are of long standing, and some have been corrected, as witness the growing replacement of "glycerine" by "glycerol," or at least "glycerin," and the use of the spelling "pyrrole." At present new natural compounds are frequently named with a characteristic suffix and so are partially systematic. The usual neutral ending (not indicating the presence of any particular function) is *-in*. (It should be noted here that the distinction between *-ine* and *-in* is not possible in German, since *e* is a sign of the plural, and is not altogether convenient in French because of gender. This is merely an illustration of the language differences of which any nomenclature must take account.)

It is natural that the first systematic organic names should have been patterned after those of inorganic compounds, especially as chemists thought in terms of the dualistic theory in the first half of the nineteenth century, when theories of organic structure were in the formative stage. Liebig and Wöhler (Annalen, 1832, 3, 261–262) introduced, in 1832, the useful suffix *-yl* in the radical name *benzoyl*. Berzelius coined the name *ethyl* the following year. According to the views of that time these "compound radicals," or stable groups of atoms, existed in their compounds in combination with a negative part, thus playing the same rôle as that of metals or ammonium in inorganic compounds. In this way originated such names as benzoyl chloride,

ethyl bromide, and ethyl acetate, completely analogous to inorganic names. This may be called the first method of forming systematic organic names.

Chemists are no longer dualists and are free to regard as a radical any portion of an organic molecule, but the idea of the radical is still indispensable in organic naming. The American Chemical Abstracts (1945, 39, 5963-5967) publishes a list of the names and formulae of over 400 radicals used in the entries of organic compounds in its indexes, and more could be added.

A second method of naming soon supplemented the first. The meanings of the terms "alcohol" and "ether" were extended to include substances chemically similar to ordinary alcohol and ether and the different alcohols and ethers were distinguished by the names of the radicals present in them; as ethyl alcohol, amyl alcohol, ethyl ether, methyl ether. In these names an analogy may be seen to the old inorganic names "copper vitriol," "iron vitriol," and to the names of biological species. The same method was also applied to compounds which are conceived as derivatives of acids, as in the names acetic ether (later acetic ester), benzoic aldehyde, butyric amide, propionic nitrile; phrases of this type also became condensed into single words, as benzaldehyde, butyramide, propionitrile.

Names formed by the above two methods are still in common use, especially for the simpler and better known compounds. The limitation on using the names of radicals in this manner is the large number of such names which would have to be coined; every organic chlorine compound, for example, can be regarded as the chloride of a different radical.

**The Substitution Method.**—A much more fruitful and elastic principle of nomenclature was suggested by the substitution theory. Since the hydrogen of methane can be replaced, step by step, by chlorine it is legitimate and convenient to think of methane as the parent compound of which the chlorine compounds are modifications. This can be indicated by the names monochloromethane or simply chloromethane for  $\text{CH}_3\text{Cl}$  instead of "methyl chloride," dichloromethane for  $\text{CH}_2\text{Cl}_2$  instead of "methyleno chloride," and trichloromethane for  $\text{CHCl}_3$  instead of "methenyl chloride." Thus one prefix, in combination with numerical prefixes, serves in place of three names of radicals. This principle of naming in terms of substitution has been widely applied, with little regard to whether the replacements indicated by the names are factually possible.

The difference between the "species" method and the substitution method of naming can be seen well in the case of the alcohols. "Methyl alcohol" and "ethyl alcohol" denote single compounds, but there are two propyl alcohols and four butyl alcohols, the radical of each of which must be distinguished in some way. When one proceeds to the amyl alcohols it becomes exceedingly inconvenient to distinguish the eight varieties as "pri-n-amyl alcohol," "pri-act-amyl alcohol," "sec-act-amyl alcohol," etc. This difficulty was relieved somewhat by the introduction of the carbinol nomenclature.

"Carbinol" is really another name for the simplest alcohol,  $\text{CH}_3\text{OH}$ , methanol or methyl alcohol, which can be considered as the parent of other alcohols. By imagining carbinol as modified by the introduction of various hydrocarbon radicals in place of one or more of the three hydrogen atoms of the methyl group one arrives at such names for the amyl alcohols as *n*-butylcarbinol, *sec*-butylcarbinol, and methylpropylcarbinol, in which the names of simpler radicals are used. Similarly, many acids may be named as derivatives of acetic acid; as, trimethylacetic acid,  $(\text{CH}_3)_3\text{C}\cdot\text{CO}_2\text{H}$ ; olefins may be named as ethylene derivatives, as *syn*-dimethylethylene; and so on.

This plan of naming compounds of more or less complex structure as substitution products of a simpler parent compound forms the basis of most present-day organic nomenclature. The parent compound must not, however, be too simple, as then the substituents may be too complex. This is why the use of such simple parent compounds as methane, carbinol, and acetic acid has only a restricted value.

A broader general basis is needed and, since organic chemistry has been defined as the chemistry of the hydrocarbons and their derivatives, it would be natural to find such a basis in the hydrocarbons.

The suffix *-ane* was already in use for certain hydrocarbons, as ethylene, when Hofmann (Jahresbericht über die Fortschritte der Chemie, 1865, 413) made the proposals that the five vowels be used to form the endings *-ane*, *-ene*, *-ine*, *-one*, and *-une* to name, respectively, hydrocarbons of the five series  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{C}_n\text{H}_{2n}$ ,  $\text{C}_n\text{H}_{2n-2}$ ,  $\text{C}_n\text{H}_{2n-4}$ , and  $\text{C}_n\text{H}_{2n-6}$ ; for example, methane,  $\text{CH}_4$ ; ethane,  $\text{C}_2\text{H}_6$ ; ethene,  $\text{C}_2\text{H}_4$ ; ethine,  $\text{C}_2\text{H}_2$ ; propane,  $\text{C}_3\text{H}_8$ ; quartane,  $\text{C}_4\text{H}_{10}$ . (This series of endings may have been suggested by Laurent's earlier proposal of *-ae*, *-ee*, *-ie*, *-oe*, *-ue* to denote stages of substitution. See Wurtz's article on "Nomenclature" in his "Dictionnaire de chimie pure et appliquée," *ca.* 1876, Tome 2, Partie 1, p. 573.) Chemists have adopted this proposal only in part and with modifications; that is to say, they have accepted *-ane* for saturated hydrocarbons (whether open-chain or cyclic), *-ene* for unsaturated hydrocarbons (in the aliphatic series the olefins), and *-ine* for acetylene hydrocarbons (but not for diolefins). The spelling *-ine* has recently been changed to *-yne* to avoid conflict with *-ine* as used to denote bases. Hofmann's endings *-one* and *-une* have never found favour. They have not proved necessary and *-one* has been pre-empted to designate ketones.

**The Geneva System.**—During most of the nineteenth century organic nomenclature grew almost wholly by accretion, each author following the lead of others or making new proposals for the compounds with which he was immediately concerned. The result was a heterogeneous mass of usage, with many poorly constructed names.

In 1892 a nomenclature congress consisting of thirty-four prominent organic chemists, representing nine European countries, met in Geneva and adopted a series of rules embodying what has since been known as the Geneva nomen-

clature (Pictet, Arch. Sci. phys. nat. 1892, [iii], 27, 485-520; Tiemann, Ber. 1893, 26, 1595-1631); for an extended commentary, see the article by A. Combes, "Chimique (Nomenclature)" in Wurtz's "Dictionnaire de chimie pure et appliquée," 1894, Supplement 2, Partie 1, pp. 1060-1076. The system was not complete, even for aliphatic compounds. Its goal of one official name for every organic compound proved impractical of realisation. Chemists made use of some of its recommendations and paid no attention to others. The Geneva system was nevertheless a notable advance. It is characterised by clearness, logic, and beauty of arrangement ("la belle ordonnance," to use Grignard's phrase) and is well adapted to systematic works. It is followed consistently in the fourth edition of "Beilsteins Handbuch der organischen Chemie." With important modifications and additions it survives in the I.U.C. system described below.

The most important features of the Geneva system are: (1) For aliphatic compounds, selection of the longest hydrocarbon chain in the compound as a basis for the name and the designation of positions on this chain with Arabic numerals. (2) Systematic use of suffixes to denote saturation or unsaturation (-ane, -ene, -diene, etc.) and functional groups (-ol, -one, -al, -oic acid, -nitrile, etc.).

The principle of the "longest chain" greatly facilitates the naming of all but the simplest compounds. Whereas eight different radical names are required for naming the amyl alcohols by the "alcohol" method or the "carbinol" method, only one (methyl) is needed by the Geneva system. The suffixes promote brevity (ethanol as contrasted with "ethyl alcohol" or "hydroxyethane") and bring out chemical relationships (butane, butene, butadiene; propane, propanol, propanal, propanoic acid).

**The I.U.C. System.**—The incomplete state of the Geneva rules and the objections to some of their features, combined with the rapid growth of the science, led the International Union of Chemistry to appoint in 1922 a Commission on the Reform of the Nomenclature of Organic Chemistry with A. F. Holleman as chairman (succeeded later by P. E. Verkade). The Definitive Report of this Commission was adopted by the Union at Liège in 1930. It has been given wide publicity (J.C.S. 1931, 1607-1616; Ber. 1932, 65A, 11-20; Rec. trav. chim. 1932, 51, 185-217, with comments by Verkade; J. Amer. Chem. Soc. 1933, 55, 3905-3925, with comments by Patterson; etc.) and seems to have met with a favourable response. The rules contained in this report, with two amendments adopted at Rome in 1938, are given below. They constitute what has come to be called (as regards organic chemistry) the I.U.C. system or I.U.C. nomenclature.

#### I.U.C. ORGANIC RULES.

##### I. General.

1. As few changes as possible will be made in terminology universally adopted.

2. For the present, only the nomenclature of compounds of known constitution will be dealt with; the question of substances of imperfectly known constitution is postponed.

3. The precise form of words, endings, etc., prescribed in the rules should be adapted to the genius of each language by the subcommittees.

##### II. Hydrocarbons.

4. The ending *ane* is adopted for saturated hydrocarbons. Open-chain hydrocarbons will have the generic name *alkanes*.

5. The present names of the first four normal saturated hydrocarbons (methane, ethane, propane, butane) are retained. Names derived from the Greek or Latin numerals will be used for those having more than four atoms of carbon.

6. Branched-chain hydrocarbons are regarded as derivatives of the normal hydrocarbons; their names will be referred to the longest normal chain present in the formula by adding to it the designations of the side chains. In case of ambiguity, or if a simpler name would result, that chain which admits of the maximum of substitutions will be selected as the fundamental chain.

7. In case there are several side chains, the order in which such chains are named will correspond to the order of their complexity. The chain having the greatest number of secondary and tertiary atoms will be considered the most complex. The alphabetic order may also be followed in such cases.

8. In the names of open-chain unsaturated hydrocarbons having one double bond the ending *ane* of the corresponding saturated hydrocarbon will be replaced by the ending *ene*; if there are two double bonds, the ending will be *diene*, etc. These hydrocarbons will bear the generic names *alkenes*, *alkadienes*, *alkatrienes*, etc. *Examples*: propene, hexene, etc.

9. The names of triple-bond hydrocarbons will end in *yne*, *diyne*, etc. They will bear the generic name *alkynes*. *Examples*: propyne, heptyne, etc.

10. If there are both double and triple bonds in the fundamental chain the endings *enyne*, *dienyne*, etc., will be used. The generic names of these hydrocarbons will be *alkenyynes*, *alkadienyynes*, etc.

11. Saturated monocyclic hydrocarbons will take the names of the corresponding open-chain saturated hydrocarbons, preceded by the prefix *cyclo*. They will bear the generic name *cycloalkanes*.

12. When they are unsaturated, rules 8-10 will be applied. However, in the case of partially saturated polycyclic aromatic compounds the prefix *hydro*, preceded by *di*-, *tetra*-, etc., will be used. *Example*: dihydroanthracene.

13. Aromatic hydrocarbons will be denoted by the ending *ene* and will otherwise retain their customary names. However, the name *phene*\* may be used instead of *benzene*.

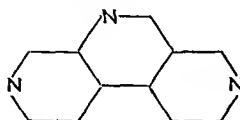
##### III. Fundamental Heterocyclic Compounds.

14. The endings of customary names, endings which do not correspond to the function of the substance, will undergo the following modifications, so far as they are in accord with the genius of each language: (a) The ending *ol* will be changed to *ole*. *Example*: pyrrole. (b) The ending *ane* will be changed to *an*. *Example*: pyran.

15. When nitrogenous heterocycles not having the ending *ine* give basic compounds on progressive hydrogenation, such derivation will be indicated by the successive endings *ine*, *idine*. *Examples*: pyrrole, pyrroline, pyrrolidine; oxazole, oxazoline.

16. The ending *a* is adopted for hetero atoms occurring in a ring. Oxygen will accordingly be indicated by *oxa*, sulphur by *thia*, nitrogen by *aza*, etc. The letter *a* may be elided before a vowel. *Examples*: thiazole, oxadiazole, thiazine, oxazine.

While the universally accepted names of heterocyclic compounds are retained, the names of other heterocyclic compounds are derived from that of the corresponding homocyclic compound by adding to it the names of the hetero atoms ending in *a*. *Example*: 2:7:9-triazaphenanthrene.



\* Not used in J.C.S.

## IV. Simple Functions.

17. Substances of simple function are defined as those containing a function of one kind only, which may be repeated several times in the same molecule.

18. When there is only one functional group, the fundamental chain will be selected so as to contain this group. When there are several functional groups the fundamental chain will be selected so as to contain the maximum number of these groups.

19. Halogen derivatives will be designated by the name of the hydrocarbon from which they are derived, preceded by a prefix indicating the nature and number of the halogen atoms.

20. Alcohols and phenols will be given the name of the hydrocarbon from which they are derived, followed by the suffix *ol*. In accordance with rule 1 names universally adopted will be retained, as: phenol, cresol, naphthol, etc.

This nomenclature may also be applied to heterocycles. Example: quinobazol.

21. In naming polyhydric alcohols or phenols, one of the forms *di*, *tri*, *tetra*, etc., will be inserted between the name of the parent hydrocarbon and the suffix *ol*.

22. The name *mercaptan* as a suffix is abandoned; this function will be denoted by the suffix *thiol*.

23. Ethers are considered as hydrocarbons in which one or several hydrogen atoms are replaced by alkoxy groups.\* However, for symmetrical ethers the present nomenclature may be retained. Examples:  $\text{CH}_3\text{O}-\text{C}_2\text{H}_5$ , methoxyethane;  $\text{CH}_3\text{O}-\text{CH}_3$ , methoxymethane or methyl ether.

24. Oxygen linked, in a chain of carbon atoms, to two of these atoms will be denoted by the prefix *epoxy* in all cases where it would be unprofitable to name the substance as a cyclic compound. Examples: ethylene oxide=epoxyethane; epichlorohydrin=3-chloro-1:2-epoxypropane; tetramethylene oxide=1:4-epoxybutane.

25. Sulphides, disulphides, sulfoxides, and sulphones will be named like the ethers,\* *oxy* being replaced by *thio*, *dithio*, *sulphinyl*, and *sulphonyl*, respectively. Examples:  $\text{CH}_3\text{SO}_2\text{C}_2\text{H}_5$ , methylsulphonyl ethane;  $\text{CH}_3\text{S}-\text{C}_2\text{H}_5$ , methylthiopropene;



1-(propylsulphinyl)butane.

26. Aldehydes are characterised by the suffix *al* added to the name of the hydrocarbon from which they are derived; thioaldehydes, by the suffix *thial*. Acetals will be named as 1:1-dialkoxymethanes.

27. Ketones will receive the ending *one*. Diketones, triketones, thioketones will be designated by the suffixes *dione*, *trione*, *thione*.

28. The name *ketene* † is retained.

29. For acids the rule of the Geneva nomenclature is retained. However, in cases where the use of that nomenclature would not be convenient the carboxyl group will be considered as a substituent group and the name of the acid will be formed by adding to the name of the hydrocarbon the suffix *carboic* or *carboxylic*, according to the language. [The Geneva rules referred to read as follows: "26. Names of the monobasic acids of the aliphatic series are derived from those of the corresponding hydrocarbons followed by the suffix *oic* ‡; polybasic acids will be named with the suffixes *dioic*, *trioic*, *tetrioic*. 27. In acids of the aliphatic series the carboxyl will be considered an integral part of the skeleton of carbon atoms."]

30. Acids in which an atom of sulphur replaces an atom of oxygen will be named according to the Geneva nomenclature. Example: ethanthioic, -thiolic, -thionic, -thioethioic. If the carboxyl is considered as a substituent the compounds will be named *carbothioic* acids. The suffix *carbothioic* will be used if it is certain that the oxygen of the OH group is replaced by sulphur; the suffix *carbothionic* if it is the oxygen of the CO group; the suffix *carbothioic* will be used if both oxygen atoms are replaced.

31. The existing conventions will be retained for salts and esters.

32. Acid anhydrides will retain their present mode of designation according to the names of the corresponding acids. For names formed in accordance with the Geneva nomenclature, the anhydrides, amidoximes, amidines, imides, and nitriles will be named like the acids by adding to the name of the corre-

sponding hydrocarbon the endings *amide*, *amidine*, *amidoxime*, *imide*, and *nitrile*, respectively, while the halides will be named by combining *chloride*, etc., with the name of the radical. Examples:  $\text{C}_2\text{H}_5\text{COCl}$ , butanoyl chloride;  $\text{C}_2\text{H}_5\text{CONH}_2$ , butanamide; etc.

If the carboxyl is considered as a substituent the endings *carbonamide*, *carbonamidine*, *carbonamidoxime*, *carbonimide*, *carbonitrile* will be used. Examples:  $\text{C}_2\text{H}_5\text{COCl}$ , propanecarbonyl chloride;  $\text{C}_2\text{H}_5\text{CONH}_2$ , propanecarbonamide; \* etc.

33. The ending *ine* is reserved exclusively for nitrogenous bases. The present nomenclature of monoamines is retained. For polyamines, the name of the hydrocarbon will be followed by the suffixes *diamine*, *triamine*, † etc.

For aliphatic compounds containing quinquivalent nitrogen the ending *ine* will be changed to *onium*. For cyclic substances containing quinquivalent nitrogen in the ring the ending *ine* will be changed to *inium*; for those with the ending *ole*, this will be changed to *olium*. Examples: pyridine, pyridinium; imidazole, imidazolium.

34 (revised). (a) Derivatives of hydrogen arsenide,  $\text{AsH}_3$ , will be named like the amides and their derivatives, with the ending *arsine*. The univalent radical  $-\text{AsH}_2$  will be designated by the prefix *arsino*.

Examples:  $\text{CH}_3\text{AsH}_2$ , methylarsine;  $(\text{CH}_3)_3\text{As}$ , trimethylarsine;  $(\text{CH}_3)_2\text{AsCl}$ , chlorodimethylarsine;  $(\text{CH}_3)_3\text{AsO}$ , trimethylarsine oxide;  $\text{H}_2\text{AsCH}_2\text{CH}_2\text{AsH}_2$ , 1:2-diaarsinoethane or ethane-1:2-diaarsine;  $(\text{C}_2\text{H}_5)_3\text{AsOH}$ , triethylarsonium hydroxide;  $(\text{CH}_3)_3\text{As}(\text{CH}_3)_2$ , tetramethylarsine.

(b) Acids of the types  $\text{RHA}_2(\text{O})\text{OH}$  and  $\text{RR}'\text{As}(\text{O})\text{OH}$  will be named *arsinic acids*; those of the type  $\text{RA}_2(\text{O})\text{OH}$  will be named *arsonic acids*. The radical  $-\text{AsO}_2\text{H}$  will be designated by the prefix *arsinio*, the radical  $-\text{AsO}_2\text{H}$  by the prefix *arsono*.

Examples:  $(\text{CH}_3)_2\text{AsO}_2\text{H}$ , dimethylarsinic acid;  $\text{C}_6\text{H}_5\text{AsO}_2\text{H}$ , benzenearsonic acid.

(c) Rules a and b are applicable to the analogous compounds of phosphorus and antimony, the syllable "ars" being replaced respectively by *phosph* or *stib*.

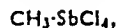
(d) The following list includes the prefixes and suffixes applicable to the most common compounds of phosphorus, arsenic, and antimony:

Radical.	Prefix.	Suffix.
$-\text{AsH}_2$	arsino	arsine
$-\text{AsO}$	arsono	
$-\text{AsO}_2$	arso	
$>\text{As}(\text{O})\text{OH}$	arsinio	arsinic
$-\text{As}(\text{O})(\text{OH})_2$	arsono	arsonic
$-\text{As}-\text{As}-$	arseno	
$-\text{PH}_2$	phosphino	phosphino
$-\text{PO}$	phosphoro	
$-\text{PO}_2$	phospho	
$>\text{P}(\text{O})\text{OH}$	phosphinio	phosphinic
$-\text{P}(\text{O})(\text{OH})_2$	phosphono	phosphonic
$-\text{P}-\text{P}-$	phosphoro	
$-\text{P}-\text{N}-$	phosphazo	
$-\text{P}-\text{As}-$	phospharseno	
$-\text{SbH}_2$	stibino	stibine
$-\text{SbO}$	stiboso	
$-\text{SbO}_2$	stibo	
$>\text{Sb}(\text{O})\text{OH}$	stibinio	stibinic
$-\text{Sb}(\text{O})(\text{OH})_2$	stibono	stibonic
$-\text{Sb}-\text{Sb}-$	antimono	
$-\text{Sb}-\text{As}-$	stibarseno	

(e) Derivatives of bismuthine,  $\text{BiH}_3$ , will be named like the arsines.

(f) Compounds of arsenic, phosphorus, antimony, and bismuth which can not be named clearly by the preceding rules will be named as derivatives of arsine, phosphine, stibine or bismuthine or (if possible) as organometallic derivatives (rule 48).

Examples:  $\text{CH}_3\text{BiO}$ , methylbismuth oxide;



methylantimony tetrachloride;  $(\text{C}_6\text{H}_5)_2\text{AsOC}_2\text{H}_5$ , ethoxydiphenylarsine;  $(\text{CH}_3)_2\text{AsOH}$ , hydroxydimethylarsine or dimethylarsenic hydroxide;  $\text{CH}_3\text{SbS}$ , methylantimony sulphide;  $(\text{CH}_3)_3\text{As}_2\text{O}$ , bis(dimethylarsenic) oxide or cacodyl oxide.

35. Compounds derived from hydroxyamine by replacement of the hydrogen of the hydroxyl will be

\* The use of butyryl (not propanecarbonyl) chloride, etc., is retained in J.C.S.

† J.C.S. retains the use of ethylenediamine, phenylenediamine, and naphthylenediamine.

\* This method is not used in J.C.S. but would be allowed for new or uncommon compounds of these types.

† J.C.S. insists on *keten*.

‡ J.C.S. uses "carboxylic" where practicable.



regarded as alkoxy derivatives; those in which an atom of hydrogen of the  $\text{NH}_2$  group is replaced, as alkylhydroxylamines. Oximes will be named by adding the suffix *oxime* to the name of the corresponding aldehyde, ketone, or quinone. *Examples*:  $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NH}_2$  ethoxyamine;  $\text{C}_2\text{H}_5\cdot\text{NH}\cdot\text{OH}$ , ethylhydroxylamine.

36. The generic term *urea* is retained; it will be used as a suffix for the alkyl and acyl derivatives of urea. *Examples*: butylurea,  $\text{C}_4\text{H}_9\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ; butylurea,  $\text{C}_3\text{H}_7\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ . The bivalent radical  $-\text{NH}\cdot\text{C}\cdot\text{NH}-$  will be named *ureylene*.

37. The generic name *guanidine* is retained.

38. The name *carbylamine* is retained.

39. *isocyanic* and *isothiocyanic* esters ( $\text{RN}:\text{C}:\text{O}$ ,  $\text{RN}:\text{C}:\text{S}$ ) will be named *isocyanates* and *isothiocyanates*.

40. The name *cyanate* is reserved for true esters which on saponification yield cyanic acid or its hydration products. The name *sulphocyanate* will be replaced by *thiocyanate*.

41. Nitro derivatives: no change in the present nomenclature.

42. Azo derivatives: the forms *azo*, *azoxy* are retained.

43. (a) Diazonium compounds,  $\text{RN}_2\text{X}$ , are named by addition of the suffix *diazonium* to the name of the parent substance (benzenediazonium chloride).

(b) Compounds having the same empirical formula but containing trivalent nitrogen will be named by replacing diazonium with *diazo* (benzenediazohydroxide).

(c) Substances of the type  $\text{RN}_2\text{OM}$  will be named *diazotes*.

(d) Compounds in which the two nitrogen atoms are united to a single carbon atom will be designated by the prefix *diazo* (diazomethane, diazoacetic acid).

(e) The term *diazamino* is retained; however, these compounds may also be regarded as derivatives of triazene.

(f) Derivatives of the substances  $\text{H}_2\text{N}\cdot\text{NH}\cdot\text{NH}\cdot\text{NH}_2$ ;  $\text{HN}:\text{N}\cdot\text{NH}\cdot\text{NH}_2$ ;  $\text{HN}:\text{N}\cdot\text{NH}\cdot\text{N}:\text{NH}$  will be named *tetrazanes*, *tetrazenes*, *pentazdienes*, etc.

44. Hydrazines are designated by the name of the alkyl radicals from which they are derived, followed by the suffix *hydrazine*. In cases where the amino group of carbonamides is replaced by the hydrazino group, the suffix *hydrazide* will be used. Hydrazo derivatives are regarded as derivatives of hydrazine. *Examples*:  $\text{CH}_3\cdot\text{NH}\cdot\text{NH}_2$ , methylhydrazine;  $\text{C}_2\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_3\text{H}_7$ , 1-ethyl-2-propylhydrazine;  $\text{C}_3\text{H}_7\cdot\text{CONH}\cdot\text{NH}_2$ , butyrylhydrazide or propanecarbohydrazide.

45. Hydrazones and semicarbazones are named like the oximes. The term *osazone* is retained.

46. The name *quinone* is retained.

47. Sulphonic and sulphinic acids will be designated by adding the suffixes *sulphonic* and *sulphinic* to the name of the hydrocarbon.

The analogous acids of selenium and tellurium will bear the names *alkaneselenonic* and *-seleninic* acids; *alkanetelluronic* and *-tellurinic* acids.

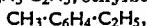
48. Organometallic compounds will be designated by the names of the organic radicals united to the metal which they contain, followed by the name of the metal. *Examples*: dimethylzinc, tetraethyllead, methylmagnesium chloride.

However, if the metal is united in a complex manner it may be considered as a substituent. *Example*:  $\text{ClHg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , chloromercuribenzic acid.

49 (revised) a. I. Cyclic hydrocarbons with all-phatic side chains are to be named according to one of the two following methods: (a) The radical names denoting the side chains are prefixed to the name of the cyclic hydrocarbon. (b) The cyclic hydrocarbon residue, if it can be named as a radical, is considered a substituent of the aliphatic chain.

Naming according to (a) is in general preferable when the side chain is short or when several side chains are present. Naming according to (b) is more convenient when the side chain is long, and particularly when the cyclic hydrocarbon residue is not at the end of this chain.

*Examples*: (a)  $\text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$ , ethylbenzene;



methylethylbenzene;  $\text{C}_{10}\text{H}_7\cdot\text{CH}:\text{CH}_2$ , ethenyl-naphthalene.

(b)  $\text{CH}_3\cdot\text{CH}(\text{C}_6\text{H}_5)(\text{CH}_2)_5\text{CH}_3$ , 2-phenyloctane;

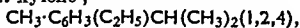
$p\text{-(CH}_3)_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ ,

3-methyl-2-(4-isopropylphenyl)heptane.

For naming cyclic hydrocarbons with side chains according to (a), it is advisable in many cases to use the common names of simple aromatic hydrocarbons.

*Examples*:  $o\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_5$ , 2-ethyltoluene;  $(\text{CH}_3)_2\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}_2(1,3,2)$ ,

2-ethenyl-*m*-xylene;



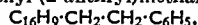
2-ethyl-*p*-cymene.

II. When several cyclic hydrocarbon residues are united by an aliphatic chain the name of the compound will be derived from that of the aliphatic hydrocarbon, provided radical names are available for the cyclic hydrocarbon residues.

*Examples*:  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ , diphenylmethane;  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{CH}_3$ , 1,2-diphenylpentane.

If this is not the case, or if the possibility of using a convenient radical name makes it desirable, the name of the compound will be derived from that of one of the cyclic hydrocarbons, on the principle of substitution.

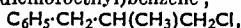
*Examples*:  $\text{C}_{14}\text{H}_9\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5(2)$ , 2-benzylantracene (better than phenyl-(2-anthryl)methane);



( $\beta$ -phenylethyl)pyrene.

b. When the cyclic hydrocarbons treated of in rule 49a carry functions which can be expressed only by a prefix, the same possibilities for names exist as those indicated in rule 49a.

*Examples*:  $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$ , 1,2-dichloro-1-phenyl-ethane or ( $\alpha\beta$ -dichloroethyl)benzene;



3-chloro-2-methyl-1-phenylpropane or ( $\gamma$ -chloroisobutyl)benzene;  $p\text{-ClC}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , 4-chloro-1-( $\beta$ -chloroethyl)benzene or 2-chloro-1-(4-chlorophenyl)-ethane.

For naming derivatives of monocyclic hydrocarbons which have common names, it will be of advantage to employ these names.

*Examples*:  $p\text{-ClC}_6\text{H}_4\cdot\text{CH}_3$ , 4-chlorotoluene (4-chloro-1-methylbenzene);  $p\text{-ClC}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ , 4- $\omega$ -dichlorotoluene (4-chloro-1-(chloromethyl)benzene, 4-chlorobenzyl chloride);  $\text{CH}_3\cdot\text{C}_6\text{H}_4(\text{NO}_2)\text{CH}(\text{CH}_3)_2(1,2,4)$ , 2-nitro-*p*-cymene (2-nitro-1-methyl-4-isopropylbenzene).

50. If it is necessary to avoid ambiguity, the names of complex radicals will be placed in parentheses. *Examples*: (dimethylphenyl)amine =  $(\text{CH}_3)_2\text{C}_6\text{H}_3\cdot\text{NH}_2$ ; dimethylphenylamine =  $\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_3)_2$ .

## V. Complex Functions.

51. For compounds of complex function, that is to say, for compounds possessing different functions, only one kind of function (the principal function) will be expressed by the ending of the name. The other functions will be designated by appropriate prefixes.

52. The following prefixes and suffixes will be used for designating the functions.

Function.	Prefix.	Suffix.
Acid and derivatives	carboxy	carboxylic, carbonyl, carbamate, etc., or oic, oyl, etc.
Alcohol	hydroxy	ol
Aldehyde	oxo, aldo (for aldehyde O) or formyl (for CHO)	al
Amine	amino	amine
Azo derivative	azo	—
Azoxy derivative	azoxy	—
Carbonitrile (nitrile)	cyano	carbonitrile or nitrile
Double bond	—	ene
Ether	alkoxy	—
Ethylene oxide, etc.	epoxy	—
Halide	halogeno (halo)	—
Hydrazine	hydrazino	hydrazine
Ketone	oxo or keto	one
Mercaptan	mercapto	thiol
Nitro derivative	nitro	—
Nitroso derivative	nitroso	—
Quinquevalent nitrogen	—	onium, inium (olium)
Sulphide	alkylthio	—
Sulphinic derivative	sulphino	sulphinic
Sulphone	sulphonyl	—
Sulphonic derivative	sulpho	sulphonic
Sulphoxide	sulphnyl	—
Triple bond	—	—
Urea	ureido	urea



53. The names of derivatives of fundamental heterocyclic substances will be formed according to the preceding rules.

#### VI. Radicals.

54. Univalent radicals derived from saturated aliphatic hydrocarbons by removal of one atom of hydrogen will be named by replacing the ending *ane* of the hydrocarbon by the ending *yl*.

55. The names of univalent radicals derived from unsaturated aliphatic hydrocarbons will have the endings *enyl*, *ynyl*, *dienyl*, etc., the positions of the double or triple bonds being indicated by numerals or letters where necessary.

56. Bivalent or trivalent radicals derived from saturated hydrocarbons by removal of 2 or 3 hydrogen atoms from the same carbon atom will be named by replacing the ending *ane* of the hydrocarbon by the endings *ylidene* or *ylidyne*. For radicals derived from unsaturated hydrocarbons, these endings will be added to the name of the hydrocarbon. The names *isopropylidene* and *methylene* are retained.

57. The names of bivalent radicals derived from aliphatic hydrocarbons by removal of a hydrogen atom from each of the two terminal carbon atoms of the chain will be ethylene, trimethylene, tetramethylene, etc.

58. Radicals derived from acids by removal of OH will be named by changing the ending *carboxylic* to *carbonyl* or, if the Geneva nomenclature is used, *alc to oyl*.

59. Univalent radicals derived from aromatic hydrocarbons by removal of a hydrogen atom from the ring will in principle be named by changing the ending *ene* to *yl*. However, the radicals  $C_6H_5$  and  $C_6H_4 \cdot CH_3$  will continue provisionally to be named *phenyl* and *benzyl*, respectively. Moreover, certain abbreviations sanctioned by usage are authorized, as *naphthyl* instead of *naphthalyl*.

60. Univalent radicals derived from heterocyclic compounds by removal of hydrogen from the ring will be named by changing their endings to *yl*. In cases where this would give rise to ambiguity, merely the final *e* will be changed to *yl*. Examples: pyridine, pyridyl; indole, indolyl; pyrrolidine, pyrrolinyl; triazole, triazolyl; triazine, triazinyl.

61. Radicals formed by removal of a hydrogen atom from a side chain of a cyclic compound will be regarded as substituted aliphatic radicals.

62. In general, special names will not be given to multivalent radicals derived from cyclic compounds by removal of several hydrogen atoms from the ring. In this case prefixes or suffixes will be used. Examples: triaminobenzene or benzenetriaminic; dihydroxypyrrrole or pyrrolediol.

63. The order in which prefixes or radicals are stated (alphabetical order or conventional order) remains optional.

#### VII. Numbering.

64. In aliphatic compounds the carbon atoms of the fundamental chain will be numbered from one end to the other with the use of Arabic numerals. In case of ambiguity the lowest numbers will be given (1) to the principal function, (2) to double bonds, (3) to triple bonds, (4) to atoms or radicals designated by prefixes. The expression "lowest numbers" signifies those that include the lowest individual number or numbers. Thus: 1:3:5 is lower than 2:4:6; 1:5:6 lower than 2:6:6; 1:2:5 lower than 1:4:5; 1:1:3:4 lower than 1:2:2:4.

65. Positions in a side chain will be designated by numerals or letters, starting from the point of attachment. The numerals or letters will be in parentheses with the name of the chain.

66. In case of ambiguity in the numbering of atoms or radicals designated by prefixes, the order will be that chosen for the prefixes before the name of the fundamental compound or side chain of which they are substituents.

67. The prefixes, *di*, *tri*, *tetra*, etc., will be used before simple expressions (for example, diethylbutanetriol) and the prefixes *bis*, *tris*, *tetrakis*, etc., before complex expressions. Examples: bis(methylamino)propane,  $CH_3 \cdot NH \cdot [CH_2]_3 \cdot NH \cdot CH_3$ ; bis(dimethylamino)ethane,  $(CH_3)_2N \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_2$ . The prefix *bi* will be used only to denote the doubling of a radical or compound; for example, biphenyl.\*

68. A catalogue of cyclic systems, with their numberings according both to the existing system and to that of A. M. Patterson, is in preparation under the auspices

of the National Research Council of the United States and of the American Chemical Society.

In order to avoid all confusion the Commission recommends placing a scheme of numbering at the head of each article.

[The catalogue referred to was published in 1940 as American Chemical Society Monograph No. 84, "The Ring Index, a List of Ring Systems Used in Organic Chemistry," Reinhold Publishing Corporation, New York.]

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\* J.C.S. uses diphenyl.

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## Comparison of the Two Systems.—

Three differences of some importance between the original Geneva system and the I.U.C. system may be pointed out: (1) In the Geneva system the carbon skeleton of an aliphatic compound is considered fundamental and fixes the numbering of any compounds derived from it; the position of side chains thus becomes more important than that of double bonds, hydroxyl groups, or carboxyl groups so far as naming and numbering are concerned. In the I.U.C. system the fundamental chain is not necessarily the longest in the molecule but is selected so as to contain the maximum number of principal functional groups (rules 18, 51). For example, by both systems succinic acid is called butanedioic acid, but whereas the I.U.C. name of ethylsuccinic acid is ethylbutanedioic acid, in the Geneva system the presence of the ethyl group lengthens the fundamental carbon chain and the name becomes "pentanoic-3-methyloic acid." (2) The Geneva Congress was divided on the method of naming compounds of complex function, referring the question to another meeting which was never held. As the Geneva rules stand they permit the presence of two or more functional suffixes in a name, and Geneva names of this type have been used. Since this is contrary to the usual practice of chemists I.U.C. rule 51 provides that only one kind of function be expressed by the ending of the name. An example: Geneva name, "ethanolal"; I.U.C. name, hydroxyethanal (for glycolaldehyde). (3) The I.U.C. system does not attempt to prescribe one official name for each organic compound. In several cases it even outlines alternative methods of naming, and it permits the retention of "terminology universally adopted" so far as such names are not considered incorrect.

In addition to the above the I.U.C. system differs on a number of particulars and covers some topics not included in the older system. In treating of heterocyclic compounds, for example, rule 16 recognises the so-called "oxa-aza nomenclature," according to which the replacement of ring carbon atoms (with their accompanying hydrogen) by hetero atoms is denoted by such prefixes as *oxa-*, *aza-*, and *thia-*.

## Order of Precedence of Functions.—

While I.U.C. rule 51 states that, for compounds of complex function, only the principal function will be expressed by the ending of the name, it fails to indicate which function shall be chosen as the principal one in any particular case. A basis for such choices would be desirable. Some indications may be drawn from usage. For example, if an acid group is present in a complex compound the latter is likely to be named as an acid; thus,  $\text{o-HO-C}_6\text{H}_4\text{CO}_2\text{H}$  is called salicylic acid or *o*-hydroxybenzoic acid and not *o*-carboxyphenol or some other name ending in *-ol*. On the other hand a compound containing the ether function is not likely to be named as an ether if any of various other functions are also present. An examination of the journal literature (Patterson, *Rec. trav. chim.* 1929, 48, 1012–1017) reveals a number of such relations, but indicates no clear order of precedence. The need for decisions in systematic compilation is evident (for one such order, see American Chemical Abstracts, 1945, 39, 5876).

**Naming of Compounds Containing Bivalent Functions.**—The naming of ethers, ketones, azo compounds and other compounds in which a bivalent functional atom or group unites two other groups presents an annoying problem, especially if the groups thus joined are different, as in ethyl methyl ether and phenylazonaphthalene (naphthaleneazobenzene).

I.U.C. rules 23 and 25 express the ether, sulphide, disulphide, sulphoxide, and sulphone functions by prefixes, thus placing them low in the order of precedence (since by rule 51 the principal function is expressed in the ending of the name). The Geneva and I.U.C. rules give satisfactory names for aliphatic ketones, but do not cover those of the cyclic series. I.U.C. rule 42 is rather noncommittal as to azo and azoxy compounds, but rule 44 treats hydrazo compounds as derivatives of hydrazine. Apparently, each bivalent function must be considered a separate problem.

## Naming of Parent Ring Systems.—

The original Geneva system did not touch this problem and I.U.C. rules 11–16 make only a beginning on it. For discussions, see Bouveault, "Châînes fermées (Nomenclature des)" in Wurtz's "Dictionnaire de chimie pure et appliquée," 1894, Supplément 2, pp. 1043–1053; Stelzner, *Literatur-Register der organischen Chemie*, 1926, 5, IX–XV; Patterson, *J. Amer. Chem. Soc.* 1928, 50, 3074–3087; Patterson and Capell, "The Ring Index," New York, 1940, pp. 20–27. The discovery of single rings of many members, complex systems containing many rings, spiro systems, and bridged systems has created many new problems in recent years. "The Ring Index" gives the formulae, various names, and numberings for the ring systems described in the literature down to 1939.

**Numbering of Ring Systems.**—The positions of substituents in the benzene ring have been indicated by the well-known prefixes *ortho-*, *meta-*, and *para-* and the adjectives *vicinal*, *symmetric*, and *asymmetric*, or their abbreviations. Additional prefixes have been used for naphthalene. The employment of Greek letters has also been common, as  $\alpha$  and  $\beta$  for naphtha-

lene,  $\alpha$ ,  $\beta$ , and  $\gamma$  for pyridino, and  $\mu$  for the middle, meso or 2 position in oxazolo. These are, however, special designations which apply only to certain of the simpler rings. Arabic numerals apply to all systems and tend to displace Greek letters even in the simpler cases.

Many ring systems, as benzene, naphthalene, anthracene, pyridine, quinoline, have generally accepted numberings, but many others have not. The scheme of Baeyer (Ber. 1900, 33, 3771-3775) for bridged ring systems has been widely used. For more recent proposals for comprehensive standardisation of numberings, see Stelzner, Kuh, Literatur-Register der organischen Chemie, 1921, 3, (1)-(100) and Patterson, J. Amer. Chem. Soc. 1925, 47, 543-561. The Patterson rules have been endorsed in part by the International Union of Chemistry; they are systematically applied in the American Chemical Abstracts indexes and in "The Ring Index" (see the preceding section).

**Stereochemical Nomenclature.**—The use of the prefixes *dextro*-, *levo*- or *laevo*-, *meso*-, and *anti*-, also of the abbreviations *d*-, *l*-, *dl*-, and *i*-, in distinguishing optical isomers is well known. To avoid the ambiguity that has resulted from Fischer's use of *d*- and *l*- to denote genetic relationship some chemists now use capital letters (small or large) in Fischer's sense (as, D-fructose or D(-)-fructose), retaining *d*- and *l*- to indicate direction of rotation only; D- and *d*- are distinguished in pronunciation as "dee" and "dextro." Recently such prefixes as *erythro*-, *threo*-, *gluco*-, *manno*-, have been used to denote the presence of configurations like like those of the corresponding sugars.

The use of *cis*-, *trans*- (originally *cis-trans*-), *syn*-, and *anti*- in connection with geometric isomerism is also well known. The prefix *allo*- has been used in a general sense to mean just "another" isomer, but has also acquired special meanings in the case of ethylenic compounds and of steroids. Similarly, *epi*- has special meanings in the carbohydrate and steroid fields.

These conventions are all no doubt useful, but they illustrate the complexity of the situation. A more general method for indicating configuration in compounds possessing two or more centres of asymmetry would seem desirable.

**Deuterium Compounds.**—Isotopes have not affected organic nomenclature except for the case of hydrogen, in which individual names have been given. Since use of the prefix deuterio- (or deuterio-) would produce longer names and tend to separate these names in indexes from the names of the corresponding compounds of ordinary hydrogen, the Committee on Nomenclature, Spelling, and Pronunciation of the American Chemical Society adopted a system modified from that of Boughton (Science, 1934, 79, 159-160). According to the Committee report (Crane, Ind. Eng. Chem., News Ed. 1935, 13, 200-201) the presence of deuterium ( $^2\text{H}$  or  $\text{D}$ ) in a compound is indicated by italic *d* and any necessary numerals.\* Examples:  $\text{CH}_3\text{D}$ , methane-*d*;  $\text{CDCl}_3$ , chloroform-*d*;  $\text{CH}_3\text{CDO}$ , acetaldehyde-*d*;  $\text{CD}_3\text{CDO}$ , acet-*d*<sub>3</sub>-aldehyde-*d*;  $\text{C}_6\text{H}_5\text{COOD}$ , benzoic acid-*d*;  $2\text{-D}_2\text{C}_6\text{H}_3\text{COOH}$ , benzoic-2,4-*d*<sub>2</sub> acid. Inorganic deuterium compounds are named in the same

manner. Compounds of tritium ( $^3\text{H}$  or  $\text{T}$ ) may be named similarly, with the use of *t* instead of *d*.\*

In 1938 the Commission on the Reform of Organic Nomenclature of the International Union of Chemistry adopted the same nomenclature, but with employment of Gothic or black-letter  $\delta$  instead of italic *d* (Union Internationale de Chimie, Comptes rendus, 1938, pp. 36-37).\*

**Compounds of Incompletely Known Structure.**—Until a complete structure has been worked out for a compound it is manifestly impossible to give it a systematic name which will express its structure completely. However, as the structure becomes partially known, or as the relations of an imperfectly known compound to derivatives of it become clear, it is convenient to use names which represent the existing state of knowledge.

An obvious and common method is the incorporation of suffixes in the trivial name to indicate the presence of one or more functions (as, tropine, tropinone); a second is the use of prefixes to denote the introduction of atoms or groups (as, methyleconine). *Iso*-, *pseudo*-, and *neo*- are useful in naming isomers. *Homo*- denotes a homologue, usually a next higher one.

A number of prefixes have been introduced for use in the analysis of a complex structure into simpler ones. *Anhydro*- denotes removal of water, usually one molecule (*dianhydro*-, removal of two molecules). *Dehydro*- means removal of hydrogen (*didehydro*-, removal of two atoms, *tetradhydro*-, removal of four atoms, etc.) *Nor*- usually means replacement of methyl groups or side chains, though in the case of norleucine it means an isomer of normal structure.

*Des*- has been used to denote the opening of a nitrogenous ring following exhaustive methylation (Willstätter, Annalen, 1901, 317, 268). More commonly, however, *des*-† or *de*- is used to indicate removal of something (*des*- seems to have been carried over into English from German and French without realisation that the common English form is *de*-). Following are some of the ways in which these prefixes are used. (1) Replacement of the named group by hydrogen: desacetyl-, desamino-, decarboxy-, desethyl-, desdiethyl-, desmethoxy-, desmethyl-, desdimethyl-, desphenyl-. (2) Replacement of hydroxyl by hydrogen: desoxy-. (3) Replacement of O by  $\text{H}_2$ : desoxo-.

#### BIOCHEMICAL NOMENCLATURE.

Certain groups of organic compounds are of special interest to biochemists. Among these are the fats, carbohydrates, proteins, enzymes, vitamins, steroids, hormones, and animal and plant pigments. As the structure of individual compounds belonging to these groups becomes known they take their place in the organic-chemical scheme and their systematic names should be formed on the same principles as for other organic compounds. However, many of them are complex, with structures either un-

\* The symbols *d*, *t*, and  $\delta$  have not been adopted for use in J.C.S.

† J.C.S. insists on *de*-, not *des*-.

known or only recently elucidated, and this fact together with their biological significance has led to special names and classifications. For the accepted nomenclature of such groups the reader is referred to the following Dictionary articles:

HORMONES, Vol. VI, 266c.

HEMIN, Vol. VI, 161a.

GLYCOSIDES, Vol. VI, 82b.

INDIGO, Vol. VI, 432d.

FISH OILS, Vol. V, 226d.

Alkaloids: Articles by E. Schlittler and G. Barger.

VITAMINS (*q.v.*).

PLANT PIGMENTS (*q.v.*; see also articles by A. G. Perkin and E. J. Cross).

Enzymes: Articles by E. F. Armstrong and G. T. Young.

For the nomenclature of carotenoids, see the Report of the Committee on Biochemical Nomenclature of the (U.S.) National Research Council, Chem. Eng. News, 1946, 24, 1235.

**Decisions of the I.U.C. Commission.**—In 1927 and 1928 the Commission on the Nomenclature of Biological Chemistry of the International Union of Chemistry adopted certain proposals of its chairman, Gabriel Bertrand, of which the following is a synopsis (full text in Union Internationale de Chimie, Comptes rendus, 1927, 1928). Terms in parentheses are the writers' explanations.

A. GLUCIDES. 1. *Oses* (monosaccharides). 2. *Osides* (glycosides). a. *Holosides* (hydrolysable saccharides). b. *Heterosides* (yielding on hydrolysis non-sugars as well as sugars). B. LIPIDES. 1. *Ternary lipides*. a. *Glycerides* (glycerol esters). b. *Cerides* (esters of higher alcohols). c. *Sterides* (esters of sterols). d. *Etholides* (from hydroxy acids). 2. *Complex lipides*. a. *Phospholipides*. b. *Phosphoaminolipides*. (1) *Glycerophosphoaminolipides*. (2) *Sphingophosphoaminolipides*. C. *PROTIDES*. 1. *Amino acids*. 2. *Proteides*. a. *Holoproteides* (yielding on hydrolysis only amino acids and ammonia). b. *Heteroproteides* (yielding amino acids and nonprotidic substances). D. *ASES* (enzymes).

The Bertrand classification was later declared to be tentative only and was not definitively adopted by the Union. Its terms have, however, had some use, especially in French literature.

In 1936 a Commission of the same title, under the chairmanship of Sir Arthur Harden, adopted provisionally the following report on *enzymes* (Union Internationale de Chimie, Comptes rendus, 1936, 43; this report also was not definitively adopted by the Union):

1. The word to which the ending *-ase*, adopted at the Warsaw Congress of 1927, is added should indicate preferably the nature of the substrate attacked (example, *peptidase*); or the mode of action of the enzyme (example, *dehydrogenase*); or a combination of the name of the substrate and the mode of action, whenever there is need to avoid ambiguity (example, *succinyldehydrogenase*).

2. The question as to the advisability of using special terms to indicate the synthetic or analytic action of an enzyme is left open.

3. The word *enzyme* designates the whole of the active complex, including the support and the activators. Coenzymes will be designated by the name of the enzyme activated, preceded by the prefix *co-* (example, *coglyoxylase*).

4. When it is desired to distinguish between the enzyme considered as a whole and the enzyme deprived of its activators, the total complex will be called *holoenzyme* and the residue, after separation of its activators, will be called *apoenzyme*.

5. Oxidation enzymes. The Commission considers it premature to establish a special nomenclature for dehydrogenases and oxidases.

#### PHYSICAL CHEMISTRY.

The nomenclature of physical chemistry is in part the nomenclature of physics. This situation makes standardisation somewhat more difficult to accomplish, as separate organisations serve the sciences of physics and chemistry. The literature of physical chemistry is replete with symbols, "effect" terms, and similar phrases for phenomena, as Raman effect, words to designate properties, specific terms used in special branches (as thermochemistry, radiochemistry, electrochemistry, colloidal chemistry, and spectroscopy), names of laws, designations for ultimate particles, etc. Of course, the physical chemist and the physicist have to deal with the elements and chemical compounds and to that very large extent their nomenclature problem is the same as that of chemists in general. A helpful book for the more physical terms is Le Roy D. Weld. "Glossary of Physics," (McGraw-Hill, New York, 1937). Specific terms suggested through the years have been indexed in Chemical Abstracts, with references to them also under the index heading "Nomenclature."

The physical chemist often has occasion to use symbols to represent quantities, relations, properties, and the like. Much work on standardisation has been done by the British Standards Institution (see Brit. Standards Inst. Publication No. 813 (1938), entitled "British Standard Chemical Symbols and Abbreviations"), by the American Standards Association, and by various less general groups. The most helpful recent published complication is the Report of a Joint Committee of The Chemical Society, The Faraday Society, and The Physical Society on Symbols for Thermodynamical and Physico-Chemical Quantities and Conventions Relating to Their Use adopted as recommended practice in The Proceedings of the Physical Society, The Transactions of the Faraday Society, The Journal of the Chemical Society, and British Chemical Abstracts (Chemistry and Industry, 1937, 56, 860-865). See also the section on "Symbols and Abbreviations" (p. 597a).

**Spellings.**—There are some differences in British and American spellings of chemical words, but these seldom cause difficulty. Examples are the spellings "sulphur" (British), "sulfur" (American), and "aluminium" (British), "aluminum" (American). Spelling differences within these countries are also encountered at times, as when one chemist accepts and applies rules affecting word endings and

another prefers to use an earlier spelling. For example, "glycerol" has not wholly supplanted "glycerine" in use.

**Word Lists.**—It is not always easy to apply rules and general principles in the determination of good nomenclature usage. A comprehensive word list, specifically designed to show approved usage, would be helpful. None exists, but because of the necessity for careful standardisation and close attention to usage in the compilation of the indexes to abstract journals and because of their extensiveness, the annual and collective indexes to British Chemical and Physiological Abstracts and to the American Chemical Abstracts are a helpful source of information as to good names for individual substances. The chemical words in Webster's New International Dictionary have been entered with due regard for nomenclature rulings. Chemists with present-day nomenclature interests and problems will find other lists and sources of help in references given in this discussion and below.

#### ADDITIONAL REFERENCES

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##### Inorganic.

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- Meyer and Rosenheim, Die Vorschläge der deutschen Nomenklaturkommission für anorganischen Chemie, Z. angew. Chem. 1925, 38, 713-715.
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A. M. P. and E. J. C.

#### LITERATURE, CHEMICAL.

Historians state that the first libraries were found in ancient Egyptian temples. The records were liturgical in form but did include material from the horretic arts, alchemy, astrology, and medicine. Two hundred years after the invention of printing the published alchemical literature consisted largely of books replete with mystic symbols. The decrease in persecution of scientists during the seventeenth century encouraged the rise of learned societies. There then developed an insistent demand for permanent, comprehensible and generally available records of their activities. Thus the general scientific journal was born and began to flourish between 1660 and 1730 (Transactions of the

Royal Society, 1665). Specialisation soon developed. The prefix *al* was dropped from the older name and the first chemical periodical was started (Croll's *Chemisches Journal*, 1778). Later journals appeared devoted to pure and to applied chemistry. Further subdivision began about 1860 with the publication of journals confined in scope to special phases of pure chemistry and to individual industries. Such developments are still in progress.

**Original Sources.**—To-day of the more than four thousand journals<sup>1</sup> publishing articles on chemical subjects, the most important are sponsored by the national chemical societies; many are issued by government bureaux and other institutions; a few are purely business ventures. Among the last may be included "trade" organs, each frankly issued to promote the sale of some commodity through the publication of pertinent information (*e.g.*, Bulletin of the Tin Research Institute).

Another form of basic literature is the patent. Leading governments of the world, recognising the results of mental effort as intellectual property, have established legal restrictions to its use. Details vary with the country but two forms are generally affected. Literary and artistic products acquire protection by copyright. New and useful discoveries or inventions are safeguarded by letters patent. The application for a patent must contain a disclosure of the idea claimed patentable. If allowed, the patent office publishes a brief announcement of the grant, and provides ways for the acquisition of complete copies by interested parties.<sup>2</sup>

A patent is granted ostensibly to reward the meritorious inventor but actually to protect the exploiter. Consequently the document is written in a manner to secure maximum protection for minimum disclosure. Furthermore it presupposes an intimate acquaintance with the prior art and legal practice in phraseology, therefore is not easily comprehended by the untutored. In spite of these features patents form a vitally important division of the chemical literature.

Three other forms of original reports are books, masters' and doctoral dissertations, and bulletins of governmentally and privately supported laboratories. To-day a book is seldom used as the medium for the announcement of recent discoveries because journal articles appear more promptly and probably are more widely distributed. While complete doctoral theses are filed with the proper university officials the new and essential parts are usually condensed into one or two papers and published with an explanatory footnote in some appropriate periodical. When government bulletins are treated in the same way or the agency concerned maintains its own medium, *e.g.*, the Journal of Research of the National Bureau of Standards (U.S.A. 1928+), the location of published findings is not difficult. State offices frequently issue bulletins, however, that contain valuable chemical data lost to all except those immediately related because the bulletins are not mentioned in the usual guides.<sup>3</sup>

Many lists of journals and other primary sources have been published with divers objec-

tives. In addition to union lists of periodicals<sup>1</sup> the synchronistic table<sup>2</sup> is very useful for disentangling wrong references. It correlates volume number with year of publication. Patent lists are of two sorts, official statements of government patent offices<sup>3</sup> which announce new grants and unofficial surveys<sup>6</sup> restricted in various ways. The latter secondary sources, particularly German annual summaries and technological monographs, may contain extensive tables, indexes, or bibliographies topically classified.

Book lists vary from catalogues limited geographically,<sup>7</sup> temporally,<sup>8</sup> or by subject<sup>9</sup> to the monumental "Union Catalog" in card form at the Library of Congress (Washington, D.C.), which, in addition to information about some 12 million books, indicates where a copy of each can be found. Guides to doctoral dissertations<sup>10</sup> differ likewise, while keys to government documents depend on the official attitude in the country of issue.<sup>11</sup>

One serious impediment to the use of all aids just mentioned is that while specifying author, title, pagination, publisher, and date they give very little information regarding content. The average scientifically minded person goes to the original literature for data about an idea but usually has no notion of which other investigator gathered and recorded the facts or in what surroundings he put them. Lists, therefore, at best merely help to divide sources into groups: unlikely, possible, and probable. Such aid is entirely inadequate for saving much time.

**Secondary Sources.**—Primary sources total well into the millions. In recent normal years the annual volume of the two forms, chemical articles and patents, as noted by Chemical Abstracts,<sup>12</sup> has been approximately forty and twenty thousand, respectively. They are unorganised except for the type of report to be expected in a particular journal. Consequently the first step necessary to make the information available in this volume of publication is a secondary source organised to help a searcher cull out and locate as directly as possible all of the relevant original material. Indexes arranged alphabetically according to title or author have proved to be of minor value. Subject indexes are more useful. Of even greater importance are the abstract journals. Two, the *Chemisches Zentralblatt* (1830+) and *Chemical Abstracts* (1907+) are especially helpful from the standpoint of complete coverage<sup>13</sup> of the chemical literature. Both have such coverage as a goal. They try to secure a copy of every chemical contribution and prepare an abstract, mentioning author, title, location, and nature in addition to an adequate summary of the contents in order that a reader can determine, before consulting the original paper, whether it may contain anything of interest to him. The abstracts are classified and arranged for publication according to field and form (article, book, patent, etc.) of the source material.

The *Zentralblatt* appears every week, *Chemical Abstracts* twice a month. Both journals undertake not only the preparation of abstracts but also subject, author, formula, and patent number indexes, annual and cumulated. Inexperienced people often assume that random use of

these search aids will disclose any desired data in print. This assumption is seldom entirely true. The likelihood of even partial success is far greater when the reader is familiar with the principles of construction of the index in hand, realises the difficulties inherent in the identification of an author and the problems of synonymy,\* especially where foreign languages are involved. Furthermore so called "hidden information" is not difficult to locate if one realises the importance of correlation in any literature search. When an abstract mentions experimental results it is often deemed unnecessary to reveal by direct index entry that the original article describes the apparatus, conditions, procedures, and reagents.

In 1871 the Journal of the Chemical Society (London) began to print abstracts chiefly in its own field of pure chemistry. Later (1882) the Journal of the Society of Chemical Industry started an "Abstracts" section. As time passed considerable overlapping developed so the two groups decided to unite their activities in a Bureau of Chemical Abstracts. The first issue of *British Chemical Abstracts* appeared in 1926, "Part A, Pure Chemistry" under separate cover; "Part B, Applied Chemistry" still as a section of the industrial publication. More recently (1937) the journal name was changed to *British Chemical and Physiological Abstracts*. Section A is now in three parts: I—General, Physical, and Inorganic Chemistry; II—Organic Chemistry; III—Physiology, Biochemistry, and Anatomy. Section B also has three units: I—Chemical Engineering and Industrial Inorganic Chemistry, including Metallurgy; II—Industrial Organic Chemistry; III—Agriculture, Foods, Sanitation. Section C covers Analysis and Apparatus. Appropriate indexes are supplied.

Other article journals have published abstracts at some period. Examples are:

<i>Ann. Chim. Phys.</i> . . .	1789-1870
<i>Dinglers Polytech. J.</i> . . .	1820-1931
<i>Annalen</i> . . . . .	1832-1860
<i>Bull. Soc. chim.</i> . . .	1863+
<i>Z. angew. Chem.</i> . . .	1887-1918
<i>J. Amer. Chem. Soc.</i> . . .	1897-1906
<i>Chim. et Ind.</i> . . . .	1919+

Many still do include them. This is particularly true of the more specialised publications such as the Journal of the Iron and Steel Institute (1871+) and Journal of the Society of Dyers and Colourists (1884+). In related fields *Science Abstracts*, A, covers physics (1903+), and *Physiological Abstracts* (1916-1937) deals with biochemistry.

Early in the development of modern chemistry scientists realised the difficulty of keeping themselves abreast of the advances in all branches. Consequently annual survey series were started. One of the most important was Liebig and Kopp's "*Jahresbericht* . . ." (1847-1910). Many of these series ceased publication long ago but good ones are still being issued. Among the better known are the *Annual Reports of the Chemical Society* (London, 1904+) and the

\* *E.g.*, in this Dictionary material on the *Weathering of paint* will be found under the heading *Ageing*.



Applied Chemistry Reports of the Society of Chemical Industry (1916+). They are critical and, of necessity, brief, but give adequate references to the original work. The reviewers are active experts in their respective fields.

Some review books are available covering particular subjects. An example is S. Glasstone's "Recent Advances in Physical Chemistry," Churchill, 1936. The journal, *Chemical Reviews* (1924+) contains articles devoted to special topics. The reference lists are usually important and carefully selected. Many periodicals feature review articles, especially at the turn of the year.

Similar to reviews in purpose, although more detailed in treatment, are the monograph series, some of which cover the entire field of science, as the *Actualités scientifiques et industrielles*. Others are confined to one branch, e.g., American Chemical Society Monograph Series; while still others are restricted to a single subdivision as *Die Chemische Analyse*, and the *Monographs on Biochemistry*. Individual titles are not easily located in libraries cataloging unanalysed series unless it is remembered to first look for the series title.

**Reference Books.**—The next step in the process of condensing chemical information yields encyclopædias and dictionaries. These names are used somewhat interchangeably and may not accurately describe the books to which they are applied. This Dictionary is encyclopædic in many parts. F. Ullmann's "Enzyklopädie der technischen Chemie," 10 vol. and Index,\* Berlin, 1928-32, is similar but places more emphasis on the patent literature, while H. von Fehling's "Neues Handwörterbuch . . .," 10 vol., Vioweg, 1871-1930, is outstanding for its bibliographies.

In addition to the comprehensive works there are many books more restricted in field: "Hatch's Chemical Dictionary," 3rd ed., Blackiston, 1944, by J. Grant, is useful for general quick reference. W. Gardnor's "Chemical Synonyms and Trade names," Van Nostrand, 1937; A. Macz and R. W. Paul's "Dictionary of Color," McGraw-Hill, 1930; "Merek's Index" of pharmaceuticals, Merek and Co., Rahway, N.J., 1940; and A. E. Dunstan *et al.*, "The Science of Petroleum," 4 vols., Oxford, 1938, give some idea of the range of special topics.

Bilingual and polyglot dictionaries include A. M. Patterson's "German-English Dictionary for Chemists," 2nd ed., Wiley, 1935, and its French-English counterpart, 1921; A. W. Mayer's "Chemisches Fachwörterbuch, Deutsch, Englisch, Französisch . . .," 3 vols., Spamer, 1929+; Ten Besch', "Viertallig Technisch Woordenboek," Kluwer, Deventer, 4 vols. 1925-30,† and "Pitman's Technical Dictionary of Engineering and Industrial Sciences . . .," 4 vols., London, 1928-32, in seven languages: English, French, Spanish, Portuguese, Italian, Russian, and German. Helpful as they are in the majority of cases these aids often fail to indicate the finer shades of meaning and idiom essential for an accurate translation. The larger

one-language dictionaries. (Oxford, Webster's . . .) must then be consulted.

The small one- and two-volume handbooks and recipe books are popular among industrial chemists, owing in part to the wide variety of data included in each type. Some of these books are revised annually, others at irregular intervals. Practically all have outgrown the original pocket size. A few examples are:

- F. W. Atack and E. Hopo, "Chomist's Year Book," London, 1944.
- C. D. Hedgman and H. N. Holmes, "Handbook of Chemistry and Physics," 29th ed., Chemical Rubber Publishing Co., Cleveland, 1945. (New editions published at frequent intervals.)
- H. Bennett, "Chemical Formulary," 1934+, Vol. 6, 1943.
- R. Biedermann, "Chomiker - Kalender," Springer, 1880+.
- G. S. Brady, "Materials Handbook," 5th ed., McGraw-Hill, 1944.
- R. T. Kent, "Mechanical Engineers' Handbook," 11th ed., 2 vols., Wiley, 1936-38.
- N. A. Lange, "Handbook of Chemistry," 5th ed., Sandusky, Ohio, 1914.
- J. H. Perry, "Chemical Engineers' Handbook," rev. 2nd ed., McGraw-Hill, 1944.
- S. W. Woolley and G. P. Forrester, "Recipes for the Colour, Paint, Varnish, Oil, Soap, and Drysaltery Trades," 10th ed., 1934.
- E. Midgley, "Technical Terms in the Textile Trade," 2 vols., Emmott and Co., 1931.

Related in purpose to the preceding group is a long list of books arranged in dictionary form which describe commercial chemicals, manufacturing equipment, sources of materials, specifications, etc. The following titles indicate the range:

- "British Chemicals and Their Manufacturers." An official directory covering chemicals, their trade names, uses, and makers. See "Thomas' Register" for American first hands.
- "Chemical Engineering Catalog." Published annually. American equipment, uses, etc. Also contains a frequently revised bibliography of 2,500-3,000 entries.
- T. C. Gregory, "Uses and Applications of Chemicals and Related Materials," Reinhold, 1939.
- National Research Council (U.S.A.), "Industrial Research Laboratories in the United States . . .," 7th ed., Washington, 1940.
- D. M. Nowitt, "Chemical Industries," 14th ed., London, 1940. Describes materials of construction, plant equipment and assembly, raw materials, and heavy chemicals. Cf. *Chemical and Metallurgical Engineering*. For several years this journal has been publishing flow sheets of the process industries.

Dictionaries of biography deserve consideration before leaving the alphabetised form of source book. In addition to dates of birth and death, education and honours some of these rolls include livelihood and a more or less complete

\* The first supplement appeared in 1934 under the title "Jahresberichte über die Patente und die technische Literatur der Industrieländer."

† Plus an index announced more recently.



list of the writings of each subject. The last is an important feature of J. C. Poggendorff's "Biographisch-literarisches Handwörterbuch . . .", Verlag Chemie, issued in six series down to 1931. It mentions almost all people eminent in scientific fields. If an interesting publication is discovered reference to Poggendorff should disclose every book and article by the same noteworthy scientist down to the date of the listing.

The Who's Who form of register is usually compiled on a geographical or occupational basis and is confined to living people. Examples are: "Who's Who" (chiefly British), "Who's Who in America," "American Men of Science," "Who's Who in Engineering," "Chemical Who's Who." Other more extensive sources give attention only to those who have finished their life work. The "Dictionary of National Biography," over sixty volumes with an epitome published in 1930, includes British celebrities while the "Dictionary of American Biography," twenty volumes plus an annual supplement, lists about 14,000 Americans. There are similar compilations for people of other countries.

**Bibliographies.**—An important factor in the success of any research work is a good foundation, a background of what already has been accomplished and the methods employed. They indicate the data to be checked under local conditions, the experimental direction, and, above all, the exact position and end of the path that is to be extended. Before breaking new ground, therefore, the experienced investigator first orients himself by reading encyclopædia articles, textbooks, and other broad surveys. He then seeks, and often finds, a bibliography already compiled that may be quickly brought down to date. This eliminates time wastage through needless repetition of library work already well done.

One of the best guides to published bibliographies is C. J. West and D. Berolzheimer's "Bibliography of Bibliographies on Chemistry and Chemical Technology," National Research Council (U.S.A.). The main volume covers the period 1900-24. Two supplements bring it down to 1932. For the years preceding 1900 H. C. Bolton's "Select Bibliography of Chemistry," Washington, may be useful. Attention has already been directed to Fehling's "Neue Handwörterbuch . . ." in which every major entry is well documented. The lists are not critical but fairly complete for the period covered. In many of the larger handbooks concerned with subdivisions of chemistry (*vide infra*) extensive reference lists form a part of every section. Some recently published monographs on applied chemistry have citations numbering into the thousands. The Science Museum, South Kensington, London, has prepared many short bibliographies in mimeographed form. Some chemical manufacturing companies, as a part of their advertising programme, have issued long lists of references to articles discussing recently commercialised products. Lastly the catalogue cards of many libraries carry notations regarding the bibliographical features of their technical books.

**Inorganic Chemistry.**—There are at least five important extensive surveys of inorganic

chemistry. All are alike in main topic but differ in age, completeness, arrangement, and content. Each one is the best in some respects, less satisfactory in others. The titles are:

J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 16 vols., Longmans, 1922-37.

J. N. Friend (ed.), "Textbook of Inorganic Chemistry," 11 vols. (in 21), Griffin, 1914+.

P. Pascal (ed.), "Traité de chimie minérale," 12 vols., Masson et Cie., 1931-34.

Abegg, Auerbach, and Koppel, "Handbuch der anorganischen Chemie," 4 vols. (in 13, Hirzel, 1905+).

"Gmelins Handbuch der anorganischen Chemie," 8th ed., edited by R. J. Meyer, 4 vols., completed, parts of 13 others issued, Verlag Chemie, 1924+.

The sequence of subjects in all of these books adheres in one way or another to that of the elements in the periodic table. The element and its properties are usually discussed first. There then follows a description of its compounds with all elements previously considered. Abegg's Handbuch is the oldest, least complete but most critical. Each division was compiled by a well-known authority on his subject. The numerous reference lists, often chronologically arranged, are still very useful. Friend's Textbook is in reality a series of self-sufficient monographs. Each can be revised as advances in the field warrant and new titles can be introduced without revision of the set. Some volumes are already in the third edition. Mellor's Treatise is the only book of the group written by one person. This gives it a continuity and unitary point of view not possessed by any of the others. The reference lists at the end of each chapter are keyed topically to the text. This feature occasionally causes trouble in the location of a specific citation. This difficulty has been practically eliminated in Pascal's Treatise compiled during a remarkably short period of time without suffering in quality. Some of the discussions in his book are the best in any language. If and when completed Gmelins handbook will be the most extensive and the finest reference work of the group. It includes not only inorganic chemistry but also analytical properties and, for some of the commercially important elements, an extensive survey of the patent literature. The systematic arrangement makes an index unnecessary.

There is no adequate key to the literature of inorganic chemistry, M. K. Hoffmann's "Lexikon der anorganischen Verbindungen," Barth, is a formula index good down to 1910 but there is a gap from that date to 1920, when Chemical Abstracts started to publish an annual formula index.

On the subject of inorganic laboratory work the most recent comprehensive survey is A. Stähler's "Handbuch der Arbeitsmethoden in der anorganischen Chemie," De Gruyter, Leipzig, a four-volume set published in 1913-26. It includes plans for the construction of a laboratory, discusses equipment, and considers many inorganic processes. In addition to this book there are a few one-volume manuals deal-

ing with inorganic preparations, but the literature is not as well assembled as it could be. Perhaps the recently started series, "Inorganic Syntheses," will improve the situation.

**Organic Chemistry.**—The literature of organic chemistry and the keys to that literature are probably better organised than those of any other subject. This is due chiefly to two monumental compilations, "Beilsteins Handbuch der organischen Chemie" (Springer), and M. M. Richter's "Lexikon der Kohlenstoffverbindungen" (Voss, Leipzig), plus its supplements. The 4th ed. of Beilstein, Main Series, Vols. I–XXVII, is a summary of the non-theoretical literature on all acyclic, isocyclic, and heterocyclic compounds described before 1910. The First Supplement deals with the period 1910–19 while the Second Supplement\* covers the next decade. Two index volumes for the Main Series and First Supplement are available. Vol. XXVIII is a subject key and Vol. XXIX is a formula guide. In addition two small portions of the material on naturally occurring compounds and substances of partly known composition have been released in Vols. XXX and XXXI. Beilstein is arranged on the basis of structural formulae, from the simplest to the most complex, from saturated to the most unsaturated, and contains a description of every known compound, its synthesis and properties as well as references to the original literature. This compendium of over 200,000 substances is unquestionably the most important in organic chemistry.

Richter's Lexikon is a "systematic compilation of the carbon compounds arranged according to their empirical formulæ." While some data regarding properties are given the chief value of this index is in its service as a guide to the original literature. The third edition of four volumes includes all compounds described before 1910. Stelzner's supplement in five volumes covers the period 1910–21. Later additions comprise the formula indexes of the *Chemisches Zentralblatt*.

In 1935 the first volume of Victor Grignard's "Traité de chimie organique" (Masson et Cie.) appeared. This treatise was planned to summarise in 15 volumes the various phases of organic chemistry under such topics as analysis, optical properties, saturated hydrocarbons, and organometallic compounds. About 12 volumes have appeared. A similar treatise in English but limited in scope is H. Gilman's "Organic Chemistry," 2nd ed., 2 vols., Wiley, 1943. The English version of V. von Richter and R. Anschütz "Chemistry of the Carbon Compounds," 3 vols. in 4,† Blakiston, 1934–, has long been a favoured reference text.

There are at least three important books dealing with synthetic organic chemistry. Houben-Weyl's "Die Methoden der organischen Chemie," 3rd ed., 4 vols., Thiemo, Leipzig, 1925–41, describes all general operations (halogenation, nitration, sulphonation . . .) and many specific applications of each. H. J. L. Moyer's "Lehrbuch der organisch-chemischen Methodik," 3 vols. in 6, Springer, 1933–41, was started as a

single volume on analysis and constitution, the fifth edition of which appeared in 1938. Volume II, 1933, describes the qualitative and quantitative analysis of organic compounds while Volume III, 4 parts, 1938–41, deals with the synthesis of all more important compounds. In 1921 American organic chemists issued the first volume of "Organic Syntheses" (Wiley), now well established as an annual publication of tested methods. These are cumulated every ten years to form a carefully indexed book of approximately two hundred procedures. A more recent venture is "Organic Reactions," Vol. 1, Wiley, 1942–, edited by Roger Adams.

Organic chemistry is concerned largely with the spatial arrangement of carbon atoms and various substituents. As the structures become more complex a name based on the configuration of a particular substance can vary with the point of view. In order to avoid confusion definitive aids have been published. "The Ring Index" by A. M. Patterson and L. Capell, Reinhold, 1940, contains over 4,000 parent ring systems with preferred names, numberings, and references. Each structure is assigned a number. If this key is generally adopted no uncertainty can arise in any particular discussion regarding the specific compound under consideration. The same numbering idea is used to identify dyes in F. M. Rowe's "Colour Index," Society of Dyers and Colourists, 1924–25, and G. Schultz's "Farbstoff Tabellen," 7th ed., Leipzig, 1929–, both of which systematically list the names, constitution, preparation, reactions, and literature of commercially important dyes.

**Biochemistry.**—The branch of organic chemistry known as bio- or biological chemistry has many subdivisions. Some of them are revealed by the following brief list of reference books, the two first mentioned being basic for the field.

E. Abderhalden, "Biochemisches Handlexikon," Main vols. 1–7, Springer, 1911–12; Supplemental vols. 8–14, 1914–33. Aims to discuss physical, chemical, and biochemical properties of all naturally occurring compounds.

C. Oppenheimer (ed.), "Handbuch der Biochemie des Menschen und der Tiere," 2nd ed., 9 vols., Jena, 1923–27; 1st Supplement, 1 vol., 1930; 2nd Supplement, 3 vols. in 4, 1933–36. The bibliographies are especially important.

R. E. Buchanan and E. I. Fulmer, "Physiology and Biochemistry of Bacteria," 3 vols., Williams and Wilkins, 1928–30. See reference lists.

H. Euler, "Chemie der Enzyme," 3 vols. in 6, Munich, 1925–. Widely used.

C. Oppenheimer, "Die Fermente . . .," 5th ed., 4 vols. in 5, Leipzig, 1925–29; 1st Supplement, 2 vols., 1935–39; 2nd Supplement, 1939, "Bibliographie 1924–38." The most exhaustive study on ferments in print.

A. W. Bömer *et al.*, "Handbuch der Lebensmittelchemie," 9 vols., Springer, 1933–. An exhaustive treatise on the chemistry of foodstuffs.

\* Vols. I–VI of this supplement have been published.

† The section on heterocyclic compounds is lacking.

- A. L. Winton and K. B. Winton, "Structure and Composition of Foods," 4 vols., Wiley, 1932-39.
- A. Hcffer and W. Heubner (ed.), "Handbuch der experimentellen Pharmakologie," 3 vols. in 7, Springer, 1920-35, 9 supplemental vols., 1935+. A detailed survey.
- E. Abderhalden (ed.), "Handbuch der biologischen Arbeitsmethoden . . .", 72 vols. in 107 plus a Schlusswort (Berlin and Vienna). Exhaustive discussion of biological, biochemical, and clinical diagnostic methods all well documented.

**Analytical Chemistry.**—In earlier days whenever a problem of identification or constitution arose in the field of analytical chemistry only major constituents were desired. To-day everyone realises the importance of trace elements. The presence or absence of a few parts per million of some substance may profoundly affect reaction rates, equilibria, apparent properties. Naturally the literature reveals this trend as well as the scope of analytical procedures and problems. Unfortunately there is no Beilstein of analytical chemistry. The nearest approach is a book now used infrequently, viz., A. Rüdtsile's "Nachweis, Bestimmung und Trennung der chemischen Elemente," Drechsel, Berne. Started in 1913 this comprehensive survey was planned to occupy nine volumes but the project was too great for one author. Six volumes in seven were finished during the first decade; Vol. VII, Sulphur, appeared in 1929. Supplement I, Arsenic—Beryllium, was issued in 1936. Sections on carbon, nitrogen, phosphorus, the halogens, oxygen, hydrogen, noble gases, and commercial products are still lacking. A less exhaustive summary is the W. W. Scott and N. H. Furman, "Standard Methods of Chemical Analysis," 5th ed., 2 vols., Van Nostrand, 1933, written by some fifty collaborators. Volume I considers procedures for the individual elements while Volume II deals with the analysis of commercial products and special subjects such as potentiometry, microscopy, and spectroscopy. Some of the more specialised books on analytical methods are:

- A. H. Allen, "Commercial Organic Analysis," 5th ed., 10 vols., Blakiston, 1923-33. "Properties, modes of analysis and proximate analytical examination of the various organic chemicals and products. . ."
- E. Berl and G. Lunge, "Chemisch-technische Untersuchungsmethoden," 8th ed. Main Series 5 vols. in 6, Springer, 1931-34; Supplements, 3 vols., 1939. A comprehensive summary of commercial methods for testing raw materials, process control, and assay of finished products. An English translation of an earlier edition was begun by C. A. Keane and P. C. L. Thorne in the late 1920's.
- H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," 9th ed., Washington, 1939.
- American Society for Testing Materials, Philadelphia, "1942 Book of ASTM Standards" (A Triennial Publication) I. Metals, II. Non-

metallic Materials, Construction, III. Non-metallic Materials, General. There is a 1943 Supplement to each volume.

Association of Official Agricultural Chemists, "Methods of Analysis," 5th ed., Washington, 1940. Revised every five years. The methods in this book "are accepted as authoritative in matters at issue before the (American) courts." They cover agricultural materials and foodstuffs.

In addition to the preceding, many books are available on specific methods such as electro-metric, luminescence, micro, polarographic, spectroscopic and X-ray techniques. W. Böttger's "Physikalische Methoden der analytischen Chemie," 3 vols., Leipzig, 1933-39, summaries the more important ones and gives extensive reference lists. Procedures for specific materials, e.g., brass, fats and oils, ferrous alloys, fuels, ores, sugar, water, have been published by individuals and associations. Pharmacopoeias of the different nations contain sections dealing with the assay of drugs and medicinals.

**Physical Chemistry.**—Physical chemistry is the latest main portion to be developed. This would lead one to expect a carefully and systematically compiled literature prompted and guided by experience in the other divisions. Perhaps it is yet too young for that. Actually the only comprehensive survey is K. Jellinek's "Lehrbuch der physikalischen Chemie," 5 vols., Stuttgart, 1928-33 (Part 14 of Vol. 5 was issued in 1935). A smaller book, H. S. Taylor (ed.), "Treatise on Physical Chemistry," 2nd ed., 2 vols., Van Nostrand, 1931, is now being revised with the collaboration of S. Glasstone. W. Ostwald's "Handbuch der allgemeinen Chemie," 9 vols. in 10, Leipzig, 1919-37, is really a series of monographs which the co-editors, P. Walden and C. Drucker, have striven to vitalise. The general tendency in physical chemistry has been to emphasise the subdivisions in smaller treatises of a few volumes. Some examples follow:

- J. Alexander (ed.), "Colloid Chemistry—Theoretical and Applied," 5 vols., New York, 1926-44.
- H. J. Creighton and W. A. Koehler, "Electrochemistry," Vol. I, 4th ed., Vol. II, 2nd ed., Wiley, 1943-44.
- K. J. Freudenberg (ed.), "Stereochemie," 3 vols., Leipzig, 1933.
- H. Freundlich (ed.), "Colloid Investigation Monographs," Vol. II, Leipzig, 1934. Founded by R. Zsigmondy.
- H. B. Weiser, "Inorganic Colloid Chemistry," 3 vols., Wiley, 1933-38.

An important laboratory guide is J. Reilly and W. N. Rae's "Physico-chemical Methods," 3rd ed., 2 vols., Methuen, 1940. A similar book is the Ostwald-Luther, "Hand- und Hilfsbuch zur Ausführung physikochemischer Messungen," 5th ed., Leipzig, 1931, edited by C. Drucker.

Physical constants have been assembled and published as general surveys and for individual properties. There are two outstanding examples of the first group. One has two supplements under different names.

- H. Landolt and R. Börnstein, "Physikalisch-chemische Tabellen," 5th ed., with three

supplements, 8 vols., Springer, 1923-36. The Third Supplement contains a cumulated key to the entire set.

E. W. Washburn (ed.), "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," 7 vols. and Index, McGraw-Hill, 1926-33. Undoubtedly the most complete and comprehensive résumé of numerical data in print.

C. Marie (ed.), "Tables annuelles de constantes et données numériques" (Paris). Started in 1910 the 14 volumes have appeared at irregular intervals and covered varying periods. The first five issues (1910-22) formed the basis for "International Critical Tables" and later ones serve as supplements. Two cumulated indexes cover Vols. I-V and VI-X.

N. Thon (ed.), "Annual Tables of Physical Constants and Numerical Data," Princeton, N.J., 1941+; a continuation, in looseleaf form, of the "Tables annuelles."

Surveys of individual properties have been confined to those frequently needed in the laboratory for purposes of identification or other operations. The four titles following are illustrative.

G. Egloff, "Physical Constants of Hydrocarbons," Reinhold, 1939+. Carefully selected values are given for the melting-point, boiling-point, specific gravity and refractive index of pure hydrocarbons.

I. M. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Revised edition, 3 Vols., London, 1943+.

G. H. H. Kayser, "Tabellen der Schwingungszahlen . . . Wellenlängen zwischen 2,000 Å. and 10,000 Å.," Hirzel, Leipzig, 1925. A revision with corrections incorporated by W. F. Meggers has been published by J. W. Edwards, Ann Arbor, Michigan, U.S.A., 1944.

R. Kempf and F. Kutter, "Schmelzpunkt-Tabellen zur organischen Molekular-Analyse," Vieweg, 1928.

A. Scidell, "Solubilities of Inorganic and Organic Compounds," 3rd ed., 2 vols., Van Nostrand, 1940-41.

**Industrial Chemistry.**—Industrial chemistry has many aspects. Factors in the economic success and survival of any manufacturing concern are plant location, construction, operation, and maintenance; selection, evaluation, and processing of raw materials; quality control and marketing of the final product; personnel problems and legal entanglements. Books containing the records of past activities can be very helpful not only with present problems but also in planning for the future. All phases cannot be included here but some of the more important discussions of chemical features are indicated.

E. Berl (ed.), "Chemische Ingenieur-Technik," 3 vols., Springer, 1935. Calculations, plant, and unit processes.

A. Eucken and M. Jakob (ed.), "Der Chemio-Ingenieur . . .," 3 vols. in 13, Leipzig, 1932-40. A handbook of physical processes, chemical operations and their control.

A. J. Hale, "Modern Chemistry Pure and Applied," 6 vols., London, 1921+.

A. Rogers, "Industrial Chemistry," 6th ed., Van Nostrand, 1942, edited by C. C. Furnas.

M. D. Curwen, "Chemistry in Commerce," 4 vols., London, 1937 (?).

V. Engelhardt (ed.), "Handbuch der Technischen Elektrochemie," 3 vols. in 6, Leipzig, 1931.

G. Heffter, "Chemie und Technologie der Fette und Fettprodukte," 2nd ed., 5 vols. (3 and 5 lacking), Springer, 1936+. Edited by H. Schönfeld.

G. Lange and A. C. Cummings, "Manufacture of Acids and Alkalis," 6 vols., 1923-25.

O. Bauer, O. Kröhnke, and G. Masing, "Die Korrosion metallischer Werkstoffe," 3 vols., Hirzel, 1936-41. Includes protection from corrosion.

A. Bräuer and J. D'Ans, "Fortschritte in der anorganisch-chemischen Industrie," 1921+. Vol. I, 1877-1900; Vols. II-IV, 1911-32; Vol. V, 1933-37.

P. Friedländer, "Fortschritte der Teerfarb-fabrikation und verwandter Industriezweige," Springer, 1877+. Complete text of patents in the field of coal tar chemistry. H. E. Fierz-David has edited Vol. 14 *et seq.*

J. Houben, "Fortschritte der Heilstoff-chemie," Berlin, 1926+. Part I deals with patents, 1877+.

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<sup>1</sup> Chemical Abstracts, "List of Periodicals Abstracted," American Chemical Society, Washington, 5th ed., 1936; Supplement, 1943.

Chemisches Zentralblatt, "Periodica Chémica," Verlag Chemie, Berlin, rev. ed., 1940.

"World List of Scientific Periodicals Published in the Years 1900-33," Oxford, London, 2nd ed., 1934.

W. Gregory, "Union List of Serials in Libraries of the United States and Canada," Wilson, New York, 2nd ed., 1943.

<sup>2</sup> Chemical Abstracts, 1942, 30, 11.

<sup>3</sup> F. Harden, J. Chem. Education 1944, 21, 326-335.

<sup>4</sup> J. N. Friend (ed.), "Textbook of Inorganic Chemistry," Griffin, London. A number of the volumes have tables on the preliminary pages.

Landolt - Börnstein, "Physikalisch - Chemische Tabellen," Springer, Berlin, 1923, p. 1034. Photoprint edition, Edwards Brothers, Ann Arbor, Michigan, U.S.A., 1941.

<sup>5</sup> British: The Official Journal, 1859+.

French: Bulletin officiel, 1854+.

German: Patentblatt, 1877+.

United States: Official Gazette, 1872+.

<sup>6</sup> E. Hohenloff, "Bibliography of Journals, Books and Compilations Which List and Abstract Patents," Special Libraries Association, Baltimore, Md., U.S.A., 1936.

<sup>7</sup> "The United States Catalog; Books in Print January 1, 1928," Wilson, New York, 1928. The "Cumulative Book Index," brings the Catalog down to date.

<sup>8</sup> "English Catalogue of Books," "La Librairie Française," "Halbjahrsverzeichnis . . . der deutschen Buchhandels," "Biblio" (French), "Publishers' Weekly."

- <sup>9</sup> British Science Guild, "Catalogue of British Scientific and Technical Books," 4th ed., 1934. About 13,900 titles.
- H. Bolte, "Führer durch die chemische Literatur," Hamburg, 1927.
- Chemical Engineering Catalogue, Section on "Technical and Scientific Books," New York, 1934-44.
- "Chemical Industries" (British), Section XII, Bibliography.
- <sup>10</sup> T. R. Palfrey and H. E. Coleman, "Guide to Bibliographies of Theses," 2nd ed., Chicago, 1940.
- <sup>11</sup> Great Britain: "Government Publications," 1922+; "List of Publications of the Department of Scientific and Industrial Research," H.M. Stationery Office, London.
- United States: "Document Catalog," 1893+; "Monthly Catalog of Public Documents," Government Printing Office, Washington, D.C.
- <sup>12</sup> Annual reports of the editor in Proceedings of the American Chemical Society, Official Reports for each year. Published in Chemical and Engineering News.
- <sup>13</sup> Cf. S. C. Bradford, Chemistry and Industry, 1937, 56, 947.

B. A. S.

## NOMOGRAMS (v. Vol. III, 3c, 5a).

NONANE,  $C_9H_{20}$ , is the ninth member of the homologous series of saturated aliphatic hydrocarbons,  $C_nH_{2n+2}$ . Thirty-five isomeric nonanes are possible theoretically (excluding stereoisomers) and about 24 have been described in the literature. A list has been drawn up by Francis (Ind. Eng. Chem. 1943, 35, 442) giving calculated values of boiling points, densities, and refractive indices for all isomers, together with observed values where known.

*n*-Nonane,  $CH_3[CH_2]_7CH_3$ , has b.p.  $150.71^\circ$ , f.p.  $-53.69^\circ$ ,  $\rho_4^{20}$  0.71790, and  $n_D^{20}$  1.40562. It occurs naturally in petroleum, and can be prepared as follows: oenanthol (*n*-heptaldehyde) is treated with ethyl magnesium bromide to give nonanol-3, which reacts with phosphorus and iodine to give the halogenated product; this is boiled with alcoholic potash to yield nonene, which is then hydrogenated (Mair, Chem. Zentr. 1933, 1, 402; Wibaut *et al.*, Rec. trav. chim. 1939, 58, 359).

When heated at  $475^\circ$  in the presence of  $Cr_2O_3$ -CoO and  $Al_2O_3$ - $Cr_2O_3$ -CoO catalysts, *n*-nonane is dehydrogenated and cyclised to *o*-ethyltoluene (Sergienko, Chem. Zentr. 1942, 1, 2219).

Vapour-phase nitration of *n*-nonane with nitrogen peroxide at  $200^\circ$  gives a mixture of mono- and di-nitrononanes (Urbanski and Slon, Compt. rend. 1937, 204, 870).

When heated with anhydrous aluminium chloride for 8 hours, *n*-nonane is split into butane and pentene, the latter being then transformed into cyclopentane under the influence of the catalyst (Cox, Bull. Soc. chim. 1925, [iv], 37, 1549).

B. A. K.

**NONOIC ACIDS.** The most important of the 89 possible nonoic acids of the formula  $C_8H_{17}\cdot COOH$  is *n-nonoic acid* (nonic, nonanoic, nonylic, pelargonic acid). This has been isolated from the oil of *Pelargonium roseum* (Pless, Annalen, 1846, 59, 54), from Japan wax and from fusel oils. It is conveniently prepared by the decarboxylation of heptyl malonic acid, prepared from diethyl malonate, *n*-heptyl bromide and sodium *n*-butoxide in *n*-butyl alcohol (Organic Syntheses, Coll. Vol. II, 1943,

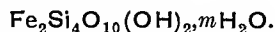
p. 474). It has also been made by the hydrolysis of octyl cyanide, by the oxidation of oleic acid (G.P. 565158) or oil of rue, by an aceto-acetate synthesis, or by fission of undecylenic acid with potassium hydroxide.

*n*-Nonoic acid has m.p.  $12.5^\circ$ , b.p.  $253-254^\circ$ ,  $\rho_4^{12.5}$  0.9109. Methyl ester, b.p.  $213-214^\circ$ , ethyl ester, b.p.  $216-219^\circ$ , anhydride, m.p.  $16^\circ$ , nitrile, b.p.  $224^\circ$ , amide, m.p.  $98.9^\circ$ , acid chloride, b.p.  $215^\circ$ , anilide, m.p.  $57.5^\circ$ , *a*-naphthylamide, m.p.  $91^\circ$ .

Passage of the acid mixed with formic acid over titanium dioxide at  $300^\circ$  gives an 85% yield of pelargonaldehyde,  $CH_3[CH_2]_7CHO$ , b.p.  $190-192^\circ$  (Sabatier and Mailhe, Compt. rend. 1912, 154, 563). The acid is converted into methyl *n*-heptyl ketone by *Penicillium glaucum* (Starkle, Biochem. Z. 1924, 151, 403), and the same ketone can be prepared by the oxidation of the sodium or ammonium salt with hydrogen peroxide (Dakin, Amer. Chem. J. 1910, 44, 46).

B. A. K.

**NONTRONITE.** A member of the isomorphous montmorillonite group (v. this Vol., p. 235d) of clay minerals,



It corresponds to montmorillonite in which the aluminium has been wholly replaced by iron ions. Its presence in clays and soil colloids can be detected by X-ray diffraction data.

D. W.

NOPAL (v. Vol. III, 226c).

NOPINENE (v.  $\beta$ -Pinene, under TERPENES).NOPINONE (v.  $\beta$ -Pinene, under TERPENES).

"NORIT" (v. Vol. I, 153a; II, 316d).

**NORMAL TEMPERATURE AND PRESSURE** ("N.T.P.") (Sometimes called "Standard Temperature and Pressure," "S.T.P.") A temperature of  $0^\circ C$ . and pressure of 1 atmosphere (76 cm. of mercury).

N.T.P. is the arbitrary reference state generally adopted for the measurement and comparison of densities and volumes of gases. The "normal" density of a gas is its mass per litre when it is at N.T.P. In practice, densities and volumes of gases are rarely measured at N.T.P., but are corrected to that state by making use of the known properties of the gas. Thus, in the case of the so-called permanent gases, it is generally sufficiently accurate to apply the ideal-gas laws, provided the gas is studied at a state not too far removed from N.T.P. If a given mass of such a gas occupies a volume  $V$  when it is at a pressure  $P$  cm. of mercury, and temperature  $t^\circ C$ ., its volume at N.T.P. would be

$$V\{273.1/(273.1+t)\}(P/76).$$

( $0^\circ C$ . being  $273.1^\circ K$ . on the absolute scale).

If the volume of a gas is measured over, for instance, water, it is, of course, necessary to allow for the partial pressure of water vapour ( $p$ ) at that temperature when reducing the gas volume to N.T.P.;  $P$ , the total pressure, is then replaced by  $(P-p)$  in the above expression. When the normal density of a gas is required very accurately, it is necessary to use the  $P$ - $V$  relations of the gas (determined experi-

mentally) rather than the ideal-gas laws when correcting to N.T.P.

The density of hydrogen at N.T.P. is 0.08988 g. per l., and that of oxygen 1.4290 g. per l. The volume occupied by 1 gram-molecular weight of any "ideal" gas at N.T.P. is 22.4 l.

N.T.P. has also been used to a small extent as a standard reference state for the compilation of the thermochemical properties of pure solids and liquids, but the modern preference for this purpose is (for practical reasons) 18°C., or 25°C., and 1 atmosphere (*cf.* F. R. Biehowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," New York, 1936).

J. A. K.

NOVOCAINE (*v.* Vol. I, 1b, 369a; II, 34b).

NUCIN, *juglone*, *regianin*, 5-hydroxy-1:4-naphthaquinone, reddish-yellow crystals, m.p. 153-154°, occurs in the shells of walnuts (*Juglans regia*) and is used as a hair dye (*v.* Vol. VI, 171b).

J. N. G.

NUCITE (*v.* Vol. VI, 495a).

NUCLEIC ACIDS. The term *nucleic acid*, originally coined to denote phosphorus-containing compounds prepared by Miescher from the nuclei of salmon sperm, has come in course of time to include not infrequently all compounds which conform to the pattern of the *nucleotide* unit. Nucleotides consist of a nitrogenous base united through a glycosidic linkage with a sugar molecule which is esterified by orthophosphoric acid. The naturally occurring nucleotides contain either a purine base (guanine, adenine, hypoxanthine), or a pyrimidine base (cytosine, uracil, thymine), or in the allied coenzymes nicotinamide or alloxazine (glycosidic link reduced). Closely related to the nucleotides are the *nucleosides*, combinations of base and sugar devoid of phosphoric acid. These are either formed by hydrolytic or enzymic dephosphorylation of the nucleotides or occur naturally; in the latter case the bases are isoguanine, uric acid, divicine or adenine. With only two exceptions (adenine thiomethyl pentoside and divicine glucoside) the sugars of the natural nucleotides are pentoses or deoxypentoses, and where examination has been adequate these are *d*-ribose and *d*-2-deoxyribose.

Although certain nucleotides occur in nature singly and as dinucleotides, those derived from guanine, adenine, cytosine, uracil, and thymine exist as complex polynucleotides of medium to high molecular weight, and it is to these compounds that the term *nucleic acid* is applied in its more limited sense. This review is concerned with these polynucleotides, but it should be realised that the differentiation is made for reasons of convenience of treatment only and is inherently unsound, since the problems encountered are generally applicable throughout the whole nucleotide field.

#### OCCURRENCE AND CLASSIFICATION.

A division of nucleic acids into two classes according to the nature of the carbohydrate (pentose and deoxypentose) resulted initially from the work of Kossel and his collaborators, who showed that the nucleic acid of yeast contained a pentose sugar (Kossel, *Arch. Anat.*

*Physiol.* 1891, 191) whereas the nucleic acid of thymus gland did not (*v. infra*) since it gave no furfural on distillation with acid (Kossel and Nenmann, *Ber.* 1893, 26, 2753). As a result of these and similar investigations it came generally to be believed that the pentose and deoxypentose nucleic acids were characteristic of, and restricted to, plant and animal cells respectively. Thus, a nucleic acid of pancreas was found to be of the deoxy-type (Levene, *Z. physiol. Chem.* 1903, 39, 4) whereas that obtained from wheat germ was a ribonucleic acid (Osborne and Harris, *ibid.* 1903, 36, 85). In 1894, however, Hammarsten (*ibid.* 1894, 19, 19) isolated two nucleoproteins from pancreas which were later shown by Steudel (*ibid.* 1907, 53, 539) to yield a deoxypentose nucleic acid and a pentose nucleic acid respectively. This threw doubt on the classification into plant and animal nucleic acids in favour at that time, and all subsequent work (*see* Gulland, *J.C.S.* 1938, 1722) has confirmed the view that both nucleic acids are characteristic of all living cells. Up to date no nucleic acid has been found to contain both pentose and deoxypentose sugars, and there are no proofs that the acids of each of the two types are similarly constituted as regards the arrangement or mode of linkage of their component nucleotides, nor in fact that all the acids of either type obtained from different natural sources are identical in the organisation of their nucleotides. Suggestions have been made that the molecules of the pentose nucleic acid of yeast and the deoxypentose nucleic acid of thymus gland are composed of polymerised tetranucleotides consisting of one of each of the four relevant nucleotides, but it is very doubtful whether this view can be held with certainty and there are no indications that the conception is of general application.

Yeast remains one of the more convenient sources of an acid of the pentose type, but such acids have also been isolated from bacteria (Coghill, *J. Biol. Chem.* 1931, 90, 57), from wheat germ (Osborne and Harris, *loc. cit.*; Clarke and Schryver, *Biochem. J.* 1917, 11, 319), from rye ergot (Gatty-Kostyal and Tesart, *Wiadom. Farm.* 1936, 63, 213, 220, 245), from pancreas (Hammarsten, Hammarsten, and Olivecrona, *Acta. Med. Scand.* 1928, 68, 215; Steudel, *Z. physiol. Chem.* 1935, 231, 273; 1936, 241, 84; Jorpes, *Acta. Med. Scand.* 1928, 68, 253; *Biochem. J.* 1934, 28, 2102), from numerous other tissues (*see* Davidson and Waymouth, *Nature*, 1943, 152, 47, for references to the occurrence of ribonucleic acid in animal tissues) and from viruses (Loring, *J. Biol. Chem.* 1939, 130, 251; Hoagland, *Ann. Rev. Biochem.* 1943, 12, 615; Stanley, *ibid.* 1940, 9, 545).

A rich source of deoxypentose nucleic acid is the thymus gland, but acids of this type are present in all tissues which have been sufficiently examined, whether of plant or animal origin. Thus they have been obtained from intestinal mucosa (Araki, *Z. physiol. Chem.* 1903, 38, 98), spleen, pancreas, and liver (Levene, *J. Biol. Chem.* 1921, 48, 177), besides numerous other animal tissues such as fish sperm, testicle, placenta, mammary gland, kidney, brain, thyroid, and erythrocyte (for references, *see* P. A.



Levene and L. W. Bass, "Nucleic Acids," Chem. Cat. Co., 1931) and are known to be present in yeast (Delaporte and Roukhelman, *Compt. rend.* 1938, 206, 1399), onion bulbs (Belozerski, *Compt. rend. Acad. Sci. U.R.S.S.* 1939, 25, 75), bacteria (Brown and Johnson, *J. Biol. Chem.* 1923, 57, 199), rye ergot (Gatty-Kostyal and Tesart, *l.c.*), horse chestnut seeds (Belozerski and Bubrovskaja, *Biochimia*, 1936, 1, 665), French and Soya bean seedlings (*idem*, *ibid.* pp. 134, 255), and other plant tissues (*see* Gulland, *J.C.S.* 1938, 1722). Deoxyribonucleic acid has been identified in only a few viruses, for example those of psittacosis (Robinow and Bland, *Nature*, 1938, 142, 720), vaccinia (Hoagland, Lavin, Smadel, and Rivers, *J. Exp. Med.* 1940, 72, 139), rabbit papilloma (Taylor *et al.*, *J. Infectious Diseases*, 1942, 71, 110), influenza and swine influenza (Taylor *et al.*, *J. Immunol.* 1943, 47, 261; 1944, 48, 129, 361; *J. Biol. Chem.* 1944, 153, 675).

It is seen, therefore, that the belief that one type of nucleic acid is characteristic of plant and the other of animal cells, is no longer tenable. As a result of the work of the last twenty years, however, the idea has arisen that deoxypentose nucleic acid is present in the nucleus, pentose nucleic acid in the cytoplasm. Feulgen, Behrens, and Mahdihassan (*Z. physiol. Chem.* 1937, 246, 203) separated the cell nucleus from the cell membrane of rye germ and showed that the nucleus contained a nucleic acid of the deoxypentose type whereas the cytoplasmic portion yielded a pentose nucleic acid (Behrens, *ibid.* 1938, 253, 185). Furthermore, Delaporte and Roukhelman (*Compt. rend.* 1938, 206, 1399) reported the presence of deoxypentose nucleic acid in the nucleus of the yeast cell and pentose nucleic acid in the metachromatic granules. This method of studying the location of the nucleic acids in the cell, however, presents serious experimental difficulties and most of the work has been carried out by histochemical methods.

The microscopic identification of the exact position of the two nucleic acids in tissues depends on two factors. First, by virtue of the purine and pyrimidine bases present in the molecules, nucleic acids of both types show selective absorption at about 2,600 Å. Second, the deoxy-sugar liberated from deoxypentose nucleic acid by acid hydrolysis is able to restore the colour to decolorised magneta, the so-called Feulgen reaction, and this does not occur in the case of the pentose nucleic acids. By measuring the absorption in the region of 2,600 Å. at different positions in the cell, a picture of the distribution of compounds containing purines and pyrimidines is obtained (Caspersson, *Skand. Arch. Physiol.* 1936, Suppl. 8). The distribution of deoxyribonucleic acid is determined by staining with Feulgen's reagent (*see* Feulgen, in *Abderhalden*, 1932, V. 2, ii, 1055). Material which shows absorption at 2,600 Å. but does not stain with Feulgen's reagent is regarded as being pentose nucleic acid, although obviously the method cannot distinguish between nucleic acid and nucleotides.

Using these methods of investigation, pentose nucleic acid has been identified in the cytoplasm

of rapidly growing tissues (Caspersson, *Nature*, 1939, 143, 602) and in the nucleolus (Caspersson and Schultz, *Proc. Nat. Acad. Sci.* 1940, 26, 507) and deoxypentose nucleic acid is found to be confined to the chromosomes (for discussion, *see* Callan, *Nature*, 1943, 152, 503). A discussion of the biological interpretation of these results has been given by Darlington (*ibid.* 1942, 149, 66).

Feulgen's reagent is frequently regarded as being specific for deoxypentose nucleic acid, but this is by no means certain, and further doubt has been cast on results obtained with it by Stedman and Stedman (*ibid.* 1943, 152, 267, 503, 557), who claim to have isolated from the chromosomes an acidic protein, chromosomin, said to form the major part of the chromosome threads. The staining of the nucleus by the Feulgen reagent is interpreted as a simple process of staining the acidic protein, chromosomin, by the basic dyestuff produced from the interaction of the Feulgen reagent and deoxypentose nucleic acid (Choudhuri, *ibid.* 1943, 152, 457), which is thought to be present not in the chromosomes but in the nuclear sap. These objections are not considered to invalidate completely the earlier conclusions (Callan, *l.c.*; Barber and Callan, *ibid.* 1944, 153, 109; Caspersson, *ibid.* 1944, 153, 499; Stedman and Stedman, *ibid.*, p. 500) and the question should be regarded at present as *sub judice*.

#### ISOLATION OF NUCLEIC ACIDS.

The main stages in the isolation of nucleic acids are the destruction of the tissues, the separation of the nucleic acid from protein, and finally the precipitation of the nucleic acid. In the preparation of both pentose and deoxypentose nucleic acids, the two former processes are commonly carried out by means of sodium hydroxide. The use of this reagent during the extraction, however, has the great disadvantage that the nucleic acid molecule may be degraded during the process of isolation. In order to avoid such decomposition, other reagents have been tried, such as sodium chloride (Clarke and Schryver, *Biochem. J.* 1917, 11, 319); in this case there are other technical objections. Heat denaturation of the protein, possibly applicable in certain cases only, proved highly successful in the isolation of the pentose nucleic acid of tobacco mosaic virus (Cohen and Stanley, *J. Biol. Chem.* 1942, 142, 863). Perhaps the most efficient method so far described for the disintegration of tissues and concomitant liberation of the nucleoprotein content of the cells is that described by Sevag and Smolens (*ibid.* 1941, 140, 883) for the isolation of bacterial nucleic acids. The bacterial cells are disrupted by ultrasonic waves, and centrifugation of the cellular debris leaves a solution containing the nucleoprotein. Nucleoproteins obtained thus are claimed to consist of covalent compounds of the two components, but in general little is known of the exact modes of union in nucleoproteins and it is possible that polar and non-polar linkages are both involved. The methods of isolating nucleoproteins and nucleic acids have been discussed by Gulland, Barker, and Jordan (*Ann. Reviews Biochem.* 1945, 14, 175).



## ISOLATION OF NUCLEOTIDES FROM NUCLEIC ACIDS.

**Pentose Nucleotides.**—On mild alkaline hydrolysis the pentose nucleic acids so far investigated yield a mixture of four nucleotides, guanylic, yeast adenylic, cytidylic, and uridylic acids. The pentose nucleic acid of yeast has been studied in most detail and in this acid the four nucleotides are stated to be present in equimolecular quantities (Levene and Jacobs, *Ber.* 1911, 44, 1027; Jones, *J. Biol. Chem.* 1916, 24, 1; Hoffmann, *ibid.* 1927, 73, 15; Kobayashi, *J. Biochem. Japan*, 1932, 15, 261; Graff and Maculla, *J. Biol. Chem.* 1935, 110, 71). This condition does not apply to other pentose nucleic acids since a higher proportion of guanylic acid is present in the pentose nucleic acid of pancreas (Steudel, *Z. physiol. Chem.* 1935, 231, 273; 1936, 241, 84; Jorpes, *Biochem. J.* 1934, 2102; Levene and Jorpes, *J. Biol. Chem.* 1930, 86, 389), and Loring (*ibid.* 1939, 130, 251) reported a 20% deficiency of purines in the nucleic acid of tobacco mosaic virus and suggested the existence of an isomeric uridylic acid.

The isolation of nucleotides from the products of hydrolysis presents some difficulty and several methods of separation are available, each possessing certain advantages (Buell and Perkins, *ibid.* 1927, 72, 21; Levene, *ibid.* 1918, 33, 425; 1919, 40, 415; Buell, *ibid.* 1913, 150, 389).

The two purine nucleotides guanylic acid and adenylic acid differ very markedly from the pyrimidine nucleotides, cytidylic acid, and uridylic acid, in their stability towards hydrolysis by acids, the former readily undergoing fission both at the glycosidic and ester linkages. The latter, however, are relatively stable and it is possible to apply this distinction in preparing the pyrimidine nucleotides from the pentose nucleic acid of yeast (Levene and Jacobs, *Ber.* 1911, 44, 1027; Thannhauser and Dorfmueller, *Z. physiol. Chem.* 1919, 104, 65; Bredereck and Richter, *Ber.* 1938, 71 [3], 718).

**Deoxypentose Nucleotides.**—Although the presence of the nucleotide pattern in deoxypentose nucleic acid was readily demonstrated, the preparation of all four nucleotides from the products of hydrolysis of this nucleic acid was a more difficult task. Levene and Mandel (*ibid.* 1908, 41, 1905) and Thannhauser and Ottenstein (*Z. physiol. Chem.* 1921, 114, 39) isolated two pyrimidine nucleotides, containing thymine and cytosine respectively, from the products of acid hydrolysis. The two purine nucleotides cannot be obtained in this way, however, because they undergo fission during this process. Furthermore, deoxypentose nucleic acid is much more stable in alkaline solution than pentose nucleic acid and could not be broken down into a mixture of nucleotides by this means. The difficulty was partly overcome by Levene and London (*J. Biol. Chem.* 1929, 81, 711; 83, 793) who split the molecule of nucleic acid enzymatically by means of intestinal juice, but the nucleotides first produced were diphosphorylated to nucleosides and also deaminated by other enzymes present. Finally, Klein and Thannhauser (*Z. physiol. Chem.* 1933, 218, 164, 173; 1934, 224,

173, 252; 1935, 231, 96) succeeded in preparing the deoxypentose nucleotides of adenine, guanine, cytosine, and thymine by the action on the nucleic acid of an extract of intestinal mucosa, in which the phosphatase was inhibited with arsenate ions and the deaminase with silver ions. These nucleotides were also diphosphorylated enzymatically to give the corresponding nucleosides. The method of isolating the adenine nucleoside from the hydrolysis product of deoxypentose nucleic acid has recently been improved (Brady, *Biochem. J.* 1941, 35, 855).

## STRUCTURE OF THE NUCLEOSIDES AND NUCLEOTIDES.

The purine nucleotides on mild acid hydrolysis yield one molecule each of phosphoric acid, *d*-ribose or deoxyribose and a purine base. The pyrimidine nucleotides are so resistant towards hydrolysis by acid that the conditions necessary for the hydrolysis of the nucleotide are sufficient to bring about further decomposition of the liberated sugar. The identifications of the purine and pyrimidine bases in the nucleotides were carried out at an early date, and for these the monograph by P. A. Levene and L. W. Bass, "Nucleic Acids," Chemical Catalogue Co., 1931, should be consulted.

The designation of the sugar as *d*-ribose in the pentose nucleotides was made by Levene and co-workers in 1909 after several other investigators had reached other conclusions. (For a summary of the literature, see Gulland and Barker, *J.C.S.* 1913, 625.)

The isolation of a pure sugar from the products of hydrolysis of the deoxypentose nucleotides proved extremely difficult. At one stage it was concluded that a hexose was concerned in the nucleotide molecule because levulinic acid was formed during acid hydrolysis; this did not, however, explain the unusual instability of the sugar. Finally, Levene and London (*J. Biol. Chem.* 1929, 81, 711) showed that the analysis of the guanine nucleoside from nucleic acid corresponded to that of a guanine deoxypentoside and that both the nucleoside and the sugar derived from it gave a positive test with Kiliani's reagent. Comparison of this sugar with synthetic *d*-2-deoxyribose showed them to be identical (Levene and Mori, *ibid.* 1929, 83, 803; Levene, Mikeska, and Mori, *ibid.* 1929-30, 35, 785). The hypoxanthine, cytosine, and thymine nucleosides, on analysis, were also found to be deoxypentosides, but as far as is known the sugars from these nucleosides have not been isolated and characterised, and they are assumed to be *d*-2-deoxyribose by analogy with guanine deoxyriboside.

The ring-structure of the sugars in the nucleosides has been shown to be of the furanose type by three distinct methods. First, the ribose of the purine and pyrimidine nucleosides, when methylated and oxidised yielded dimethoxysuccinic acid (Levene and Tipson, *ibid.* 1932, 94, 809; 97, 491; 1933, 101, 529). Second, these nucleosides and also the purine and pyrimidine deoxypentosides reacted with triphenylmethyl chloride, which was shown by Bredereck to react with a primary alcoholic

group and not with a secondary alcoholic group (Levene and Tipson, *ibid.* 1934, 105, 419; 1935, 109, 623; Bredereck, *Ber.* 1932, 65 [B], 1830; 1933, 66 [B], 198; *Z. physiol. Chem.* 1934, 223, 61). Hockett and Hudson (J. Amer. Chem. Soc. 1931, 53, 4456), however, observed that in certain sugars a secondary alcoholic group is attacked by triphenylmethyl chloride, and this invalidates, to some extent, the evidence for the furanose structure based on this method. More recently, the furanoside structures of adenosine, guanosine, and yeast adenylic acid have been confirmed by means of periodate oxidations (Lythgoe and Todd, *J.C.S.* 1944, 592).

The remaining problems in connection with the nucleotides are concerned with the union of the components. Gulland and co-workers, by comparing the ultra-violet absorption spectra of the natural nucleosides with those of appropriately substituted purine bases of known constitution, demonstrated that all known purine nucleosides are 9-substituted purines (*ibid.* 1934, 1639; 1936, 765; 1937, 1912; 1938, 692; 1939, 1369, 1784). The point of attachment of the pentose to the pyrimidine bases cytosine and uracil is the same, because treatment of cytidine or cytidylic acid with nitrous acid produces compounds identical with natural uridine and uridylic acid respectively (Bredereck, *Z. physiol. Chem.* 1934, 224, 79; Levene and Jacobs, *Ber.* 1910, 43, 3159). Uridine was methylated and subsequently hydrolysed to give 1-methyluracil (Levene and Tipson, *J. Biol. Chem.* 1934, 104, 385) thus excluding position 1 as the point of attachment of the sugar, and Hilbert and Rist (*ibid.* 1937, 117, 371), by comparing the ultra-violet absorption spectrum of uridine with that of uracil in which the hydrogen atom in position 3 and the hydrogen atom of the hydroxyl group in position 2 are substituted, showed that the sugar was attached to the pyrimidine ring at position 3. It is usually assumed, by analogy with the pyrimidine pentosides, that the deoxypentose radical substitutes hydrogen in position 3 of thymine and cytosine in the pyrimidine nucleotides, but no direct evidence on this point has been obtained.

The position of attachment of the phosphoryl group in the pentose nucleotides was at first the cause of confusion, since it was found that whereas the phosphoryl group was easily removed by acid hydrolysis from the purine pentose nucleotides of yeast nucleic acid, the closely related nucleotides inosinic and muscle adenylic acids were much more resistant to hydrolysis. Ultimately, it was shown that the phosphoryl radicals esterify hydroxyl 3 of the sugar in the purine pentose nucleotides of yeast nucleic acid (for a summary of the literature, see Gulland, *J.C.S.* 1938, 1722) and hydroxyl 5 in the more stable analogues.

Evidence as to the position of the phosphoryl radical in the pyrimidine pentose nucleotides is not as yet conclusive, except that hydroxyl 5 is free (action of triphenylmethyl chloride, Gulland *l.c.*, and synthesis, see *infra*) but the location is usually assumed to be the same as in the purine nucleotides. The problem of the position of the phosphoryl group of the deoxypentose nucleotides has not been resolved by isolation of the

sugar phosphate on account of the instability of the sugar, and this problem remains as yet unsolved.

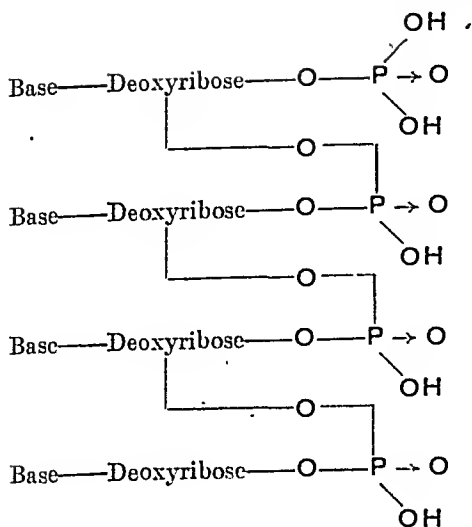
#### STRUCTURE OF POLYNUCLEOTIDES.

The data required in this connection are (i) the molecular weight, *i.e.*, the total number of nucleotides, (ii) their relative proportions, (iii) their modes of union. An important aspect of the last mentioned is the question whether the polynucleotides are, or are not, polytetranucleotides, that is molecules formed by repeated combinations of units composed of four nucleotides, one of each of the nucleotides appropriate to the nucleic acid type, arranged in uniform sequence. This is at present a debatable subject, and the existence of tetranucleotides as chemical entities cannot be considered as proved until such substances have been satisfactorily isolated and characterised. It must also be realised that there is at present no evidence that both types of nucleic acid are identical in structure, or that the various representatives of each type derived from different sources are similarly constituted (for more detailed discussion and summary of the preceding points, see Gulland, *ibid.* 1944, 208; Gulland, Barker, and Jordan, *Ann. Reviews Biochem.* 1945, 14, 175).

*Deoxypentose Nucleic Acids.*—It has already been mentioned that by suitably controlled hydrolysis of deoxypentose nucleic acid of thymus gland four nucleotides containing respectively guanine, adenine, cytosine, and thymine may be obtained. Furthermore it has been stated by Steudel (*Z. physiol. Chem.* 1906, 49, 406) and by Levene and Mandel (*Biochem. Z.* 1908, 10, 215) that these four nucleotides are probably present in equimolecular proportions in the nucleic acids of thymus and herring roe.

As a result of claims by Levene and Jacobs and by Thannhauser and co-workers (*J. Biol. Chem.* 1912, 12, 411; *Z. physiol. Chem.* 1921, 114, 17; 1926, 161, 116) to have isolated from the products of mild acid-hydrolysis compounds having the probable structure of diphosphopyrimidine nucleosides, the molecule of deoxyribonucleic acid was assumed to consist of the four nucleotides united by ester linkages as shown in (1); at that time the molecule was thought to consist of a single tetranucleotide. This structure was in accordance with the titration of deoxyribonucleic acid by Levene and Simms (*J. Biol. Chem.* 1926, 70, 327) and by Bredereck and Köthnig (*Ber.* 1939, 72 [B], 121) who found it to be a pentabasic acid. The full interpretation of their results is not, however, feasible since molecular weights were not considered simultaneously. Bredereck and Caro (*Z. physiol. Chem.* 1938, 253, 170) have cast doubt on the existence of diphosphoric esters of pyrimidine nucleosides, but until evidence against this diester structure is found, it may be accepted tentatively as representing the mode of linkage of the nucleotides.

The molecular weight of native deoxypentose nucleic acid has not yet been fully investigated, but all observers now agree that the molecules are very large, many times greater than a single tetranucleotide. Signer, Caspersson, and Ham-



I.

marsten (Nature, 1938, 141, 122), from studies of viscosity and streaming birefringence, found the length/width ratio to be 300, and the molecular weight to lie between 500,000 and 1,000,000. These figures were corroborated by Astbury and Bell (*ibid.* 1938, 141, 747), by X-ray analysis, and by Tennant and Vilbrandt (J. Amer. Chem. Soc. 1943, 65, 424) using the ultracentrifuge. Schmidt, Pickels, and Levene (J. Biol. Chem. 1939, 127, 251) considered that deoxypentose nucleic acid consists of a mixture of molecules of varying size, the range of molecular size depending on the method of extraction. Bredereck and Jochmann, using a drastic alkaline method of preparation (Ber. 1912, 75 [B], 395), obtained a product which approximated in composition and properties to a tetranucleotide. Greenstein and Jenrette (J. Nat. Cancer Inst. 1940, 1, 77) claimed that the molecular weight, as shown by measurement of viscosity and streaming birefringence, is reversibly diminished by the presence of various salts, and the question of molecular size is complicated by reversible aggregation, since Pedersen (quoted by T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford Univ. Press, 1940, p. 443) found that the sedimentation constant was highly dependent on the concentration.

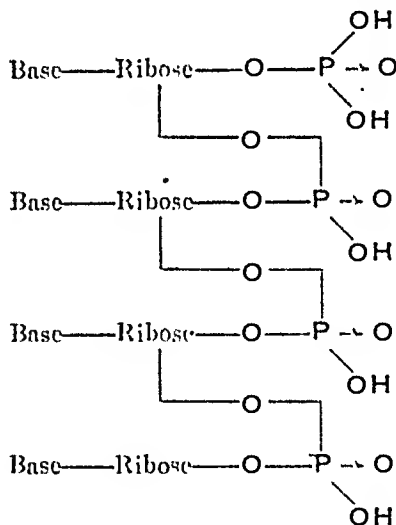
**Pentose Nucleic Acids.**—The proportions of nucleotides in different acids of this type are discussed above.

Cohen and Stanley (J. Biol. Chem. 1942, 144, 589) made a detailed study of the physical properties of the acid from tobacco mosaic virus, isolated by heat denaturation of the virus protein and thus avoiding the use of alkali; it is therefore possible that this material was, or approached closely to, the native nucleic acid of the virus. The freshly isolated acid had an approximate particle weight of 300,000 and was highly asymmetric in shape with an axial ratio about 60; it decomposed spontaneously to form still asymmetric, birefringent particles with molecular weight about 61,000. Cold alkali converted either particle into molecules with a weight of 15,000 and a length-width ratio of 10. There is at present no evidence that a unit,

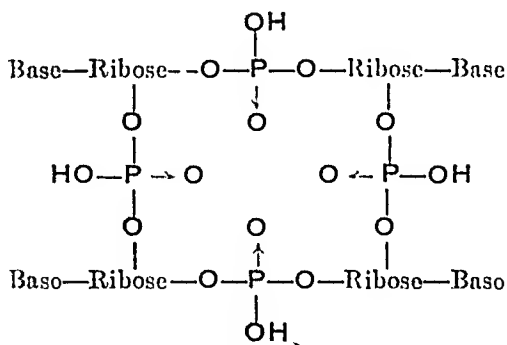
smaller than mol. wt. 15,000 but larger than a nucleotide, exists as a fundamental unit of the tobacco mosaic virus acid.

Several different structures have been suggested for the acid of yeast, only certain of which merit consideration here. Determination of the acidic groups by titration before and after alkaline fission into nucleotides shows clearly that the phosphoryl groups are concerned in the union of the nucleotides, and the interpretation of titration data necessitates also a knowledge of the molecular weight of the sample of nucleic acid used, since it seems certain that phosphoryl groups are concerned in the union of tetranucleotides to form the polytetranucleotide, if such units do, in fact, exist.

Various authors, using either electrometric titration, or titration to the phenolphthalein endpoint, found that the acid of yeast possessed either four or five acidic dissociations (Levene and Simms, *ibid.* 1926, 70, 327; Makino, Z. physiol. Chem. 1935, 232, 229; Jorpes, Biochem. J. 1934, 282, 102; Allen and Eiler, J. Biol. Chem. 1911, 137, 757; Bredereck and Jochmann, Ber. 1912, 75 [B], 395). On the basis of these results it seemed that different structures of the acid might be warranted, and indeed two formulae were proposed by Levene and Simms (II) (*l.c.*) and by Takahashi (III) (J. Biochem. Japan, 1932, 16, 463) which represented the acid as being pentabasic and tetrabasic respectively (hydrolysis of III as shown would give II).



II.

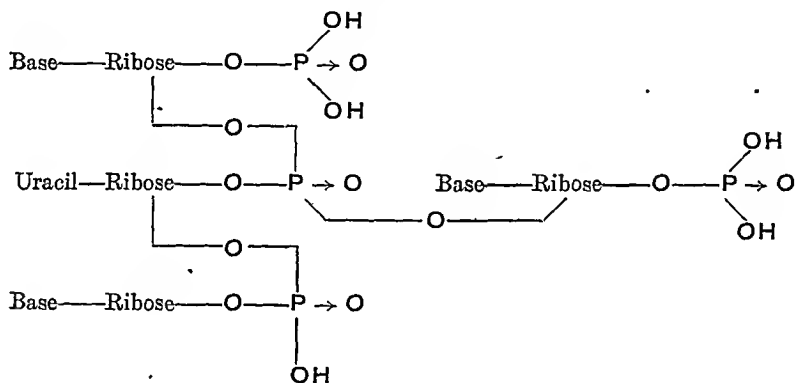


III.

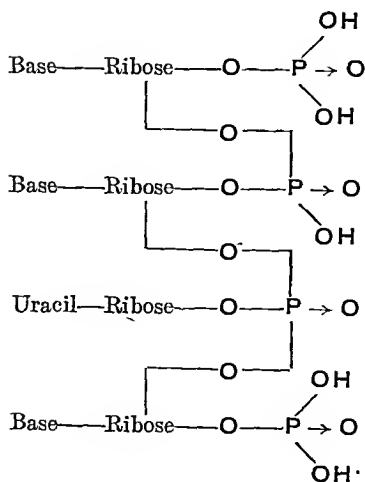
These formulæ, however, were proposed on the assumption that the molecule is a tetranucleotide as the subsequent determination of molecular weight by Myrback and Jorpes also suggested (*Z. physiol. Chem.* 1935, **237**, 159). It is now realised that the molecules are much larger, with weights varying from 10,000 to 28,000 depending on the sample and its previous treatment (Loring, *J. Biol. Chem.* 1939, **128**, *Sci. Proceedings*, **33**, 61; Fischer, Bottger, and Lehmann-Echternacht, *Z. physiol. Chem.* 1941, **271**, 246; Fletcher, Gulland, Jordan, and Dibben, *J.C.S.* 1944, 30), and some reconciliation of the discrepancies in titration data can be achieved by making allowances for differences in molecular weight of the samples examined.

Fletcher, Gulland, and Jordan (*ibid.* 1944, 33), have described detailed electrometric titrations of the acid of yeast and also of the deaminated acid prepared from it without change in molecular weight. They found that the acid exhibited four phosphoryl dissociations for each four atoms of phosphorus, three of the phosphoryl dissociations being primary and one secondary. The samples examined had molecular weights corresponding to polynucleotides

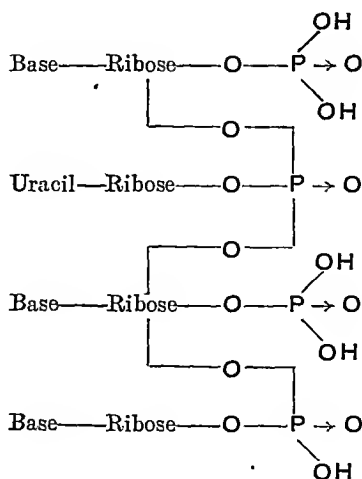
built up from 32-72 nucleotides, but mild aqueous hydrolysis of the deaminated acid liberated one additional secondary phosphoric acid dissociation for each four atoms of phosphorus, the molecular weight of the product being of the order of 1800, although the isolation of a deaminated tetranucleotide free from purine has so far proved impracticable. On the basis of these results, the formulæ (IV, V, or VI) were proposed as possible for a hypothetical tetranucleotide, and present two new conceptions. One phosphoryl group is a neutral triester. Another is a monoester, and plays no part in maintaining the skeleton of the polynucleotide; thus for the first time a feasible explanation is offered of the frequency with which low phosphorus analyses are encountered in apparently homogeneous samples of the acid. Polymerisation to a polynucleotide occurs through one of the secondary phosphoryl dissociating groups, presumably as an ester since neither hydroxyl nor amino-groups are involved; the titrations demonstrated the unsubstituted nature of the enolic hydroxyl groups of uracil and guanine, and the acids underwent deamination without diminution of molecular weight.



IV.



V.



VI.

## ACTION OF ENZYMES ON POLYNUCLEOTIDES.

Non-specific phosphomono- and phosphodiesterases were used by Gulland and Jackson (*ibid.* 1938, 1942) to throw light on the structure of yeast ribonucleic acid, and their conclusions were in agreement with those subsequently advanced (Fletcher, Gulland, and Jordan, *ibid.* 1944, 33) on the basis of electro-metric titrations (*v. supra*).

Ribonuclease, an enzyme isolated from pancreas (Jones and Perkins, J. Biol. Chem. 1923, 55, 557; Dubes and Thompson *ibid.* 1938, 124, 501; Kunitz, J. Gen. Physiol. 1940, 24, 15) and regarded as specific for ribonucleic acid, was believed to cause depolymerisation into tetranucleotides (Schmidt and Levene, J. Biol. Chem. 1938, 126, 423; Allen and Eiler, *ibid.* 1941, 137, 757) or dinucleotides (Fischer, Böttger, and Lehmann-Echternacht, Z. physiol. Chem. 1941, 271, 246; J. pr. Chem. 1911, 158, 79). Kunitz, however, found that only about half the ribonucleic acid is broken into small fragments, diffusible through cellophane, and Loring and Carpenter (J. Biol. Chem. 1943, 150, 381) concluded that a relatively large proportion of the molecule is resistant to ribonuclease and isolated small yields of the four mononucleotides after its action. The nature of the enzyme's attack on yeast ribonucleic acid is thus obscure, and it is at present unsafe to base conclusions as to structure on such experiments. The subject is reviewed by Gulland, Barker, and Jordan (Ann. Reviews Biochem. 1945, 14, 175) and by Tipson (Advances in Carbohydrate Chemistry, 1945, 1, 193).

A depolymerase of deoxypentose nucleic acid is present in calf thymus and ox pancreas (Fuegen, Z. physiol. Chem. 1935, 237, 261; 1936, 238, 105) and in extracts of the germs of Lima bean, sunflower, maize, wheat, and pumpkin (Greenstein and Jenrette, J. Nat. Cancer Inst. 1941, 2, 301; Cold Spring Harbor Symposia Quant. Biol. 1941, 9, 236); it is different from ribonuclease which has no action on deoxypentose nucleic acid. The action of the depolymerase results in disappearance of the structural or anomalous viscosity of the nucleic acid (Greenstein and Jenrette) and in an increase of acidity and conductivity (Fischer, Lehmann-Echternacht, and Böttger, J. pr. Chem. 1941, 158, 79); titration of the extra acidity suggests that the change could be a decomposition of the acid of high molecular weight into pentabasic tetranucleotides.

Cohen (J. Biol. Chem. 1945, 158, 255) has found that deoxypentose nucleoproteins as well as the nucleic acid are degraded by the depolymerase, and also that crystalline ribonuclease exhibits proteolytic activity.

## SYNTHESIS OF NUCLEOSIDES AND NUCLEOTIDES.

The complete synthesis of a nucleotide or nucleoside of either pentose or deoxypentose nucleic acid has not yet been achieved. Several nucleosides have, however, been synthesised which are related closely to those derived from ribonucleic acid, and the nucleosides obtained from yeast pentose nucleic acid by alkaline

hydrolysis have been phosphorylated to regenerate the natural nucleotides; the latter, therefore, are partial syntheses.

**Nucleosides.**—Although several methods are available for the synthesis of purino or pyrimidino glycosides, the inaccessibility of *d*-ribose and *d*-2-deoxyribose, both in the furanose form, makes the synthesis of a natural nucleoside difficult. By the interaction of an acetobromo-sugar and the silver derivative of a purino or pyrimidine, many glycosides have been prepared (for literature, see Gulland, J.C.S. 1938, 1722). Of these, the pyrimidine glycosides were much less stable towards acid hydrolysis than the natural pyrimidine nucleosides and were subsequently found to be O-glycosides. Hilbert and Johnson (J. Amer. Chem. Soc. 1930, 52, 4489), however, synthesised an analogue of uridine by the interaction of the acetobromo-sugar and diethoxypyrimidine followed by removal of the ethyl and acetyl groups.

The purine glycosides obtained by the action of an acetobromo-sugar on the 7(9)-silver derivative of the purine resemble the natural purine nucleosides in their properties, and synthetic adenine glucoside (Fischer and Helfferich, Ber. 1914, 47, 210), prepared from acetobromoglucose and silver trichloropurine, was shown by Gulland and Story (J.C.S. 1938, 250) to have the sugar attached to the purine ring at position 9, as is the case in the naturally occurring compounds. This method, therefore, provided a route to the synthesis of the natural nucleosides, since by suitable modifications the other purine nucleosides can be prepared from trichloropurine glycosides containing the appropriate sugar.

More recently Todd and co-workers have explored a new method of synthesising purine glycosides (*ibid.* 1913, 383, 386, 571; 1914, 318, 652; 1915, 556), and these researches may provide a more convenient method for the synthesis of the natural nucleosides.

**Nucleotides.**—The synthesis of pentose nucleotides has been reviewed by Gulland (*ibid.* 1914, 208).

**Analytical Methods and Metabolism.**—For analytical methods and the metabolism of nucleic acids, reviews by Allen (Ann. Reviews Biochem. 1941, 10, 221) and Loring (*ibid.* 1914, 13, 295) may be consulted.

J. M. G. and G. R. B.  
**NUPERCAINE HYDROCHLORIDE.**  
2-*n*-Butoxycinchonin- $\beta$ -diethylaminoethyl-amido. "Percaïne." Local anesthetic. B.P.C. (*v. SYNTHETIC DRUGS*).

S. E.

**NUTMEG.** The nutmeg is the kernel of the fruit of *Myristica fragrans* Houtt. (*see* MAOR, Vol. VII, 433a). When gathered the fruit is slowly dried, either in the sun or by artificial heat, the hard shell is removed and the nutmegs (except in the case of those from Ponang) washed in milk of lime. The nuts are then sorted into grades according to their size, the larger and denser being the most valuable. Those which are shrivelled are reserved for the production of ground nutmeg, of which, however, little appears on the market.

The true nutmeg is oval or nearly spherical in

shape, from 20 to 25 mm. long and from 15 to 18 mm. wide. It is wrinkled longitudinally with a groove marking the position of the raphe. In cross section it has a marbled appearance. It has a pleasant and characteristic odour and a hot aromatic taste.

Nutmeg starch is similar in appearance to the starches of the legumes and shows a well-developed cracked hilum. It is not iridescent under polarised light. Its shape is extremely irregular and it varies in size from 5 to 50 $\mu$ . A characteristic is the budded effect caused by the adherence of the smaller to the larger grains. The B.P. 1932 describes them as simple and compound grains with up to ten components, individual grains more or less rounded, up to 20 $\mu$  in diameter.

The sole use of nutmeg is as a flavouring agent, but the volatile oil is employed in medicine as an aromatic and carminative. Owing to the shortage of hashish in Egypt in recent years, nutmeg has been employed as a substitute, since the symptoms of intoxication are similar.\* The effects, however, may be much more severe and it is stated that whilst severe symptoms of poisoning may result from the consumption of half to one and a half nutmegs, death may be caused by two. The use of powdered nutmegs in cocktails has also been followed by unpleasant symptoms.

**Composition.**—The preponderating constituents are a fixed oil, starch, albuminoids, and fibre; the flavour and therapeutic action are due to the volatile oil.

According to Winton, Ogden, and Mitchell (U.S. Dept. Agric. Bureau of Chemistry, Bulletin 66, 1902), nutmeg has the composition:

	Max.	Min.
Moisture . . . . .	10.83	5.79
Ash, total . . . . .	3.26	2.13
Ash, soluble in water . . . . .	1.46	0.82
Ash, insoluble in HCl . . . . .	0.01	0.00
Ether extract, volatile . . . . .	6.94	2.56
Ether extract, non-volatile . . . . .	36.94	28.73
Alcohol extract . . . . .	17.38	10.42
Reducing matter by acid conversion (calculated as starch) . . . . .	25.60	17.19
Starch by diastase method . . . . .	24.20	14.62
Crude fibre . . . . .	3.72	2.38
Nitrogen . . . . .	1.12	1.05

Similar figures, using different methods, were published by C. Aragon, Ann. Falsif. 1915, 8, 345.

J. W. Corran and S. H. Edgar (J.S.C.I. 1933, 52, 149 $\tau$ ) have shown that nutmeg, or its oil in a concentration of 1 in 2,500, exerts practically no preservative action against fermentation by ordinary yeast. The essential oil (*v. infra* and this Vol., p. 659 $d$ ) is probably determined most satisfactorily by the method of Cocking and Middleton (Quart. J. Pharm. 1935, (VIII), 435), who record figures varying from 6.9 to 13.0% of volatile oil.

**Adulteration.**—As nutmegs are almost invariably sold whole, *i.e.*, unground, adulteration is very rare in this country.

The substitution of the Papuan (New Guinea) long nutmeg (*M. argentea*) cannot be regarded

\* Nutmeg contains nothing which shows the pharmacological action of hashish in animals, so that any reported similarity is superficial only. [Private communication from A. R. Todd.]

as legitimate, being much inferior in flavour, still less that of wild nutmegs from *M. malabarica* or other species of *Myristica*. These may be detected at once by the complete absence of aroma, and also by their different shape and size. Worm-eaten nuts may be passed off as sound after stopping the holes and coating with lime. This will be revealed by careful inspection. More or less exhausted nuts may be detected by the reduced fat content.

Small worthless nutmegs, known as grinding nutmegs, are frequently employed for this purpose, and the powder may contain curcuma, or various nut-shells. Admixture of the seed-coat (testa) may be detected by the presence of a large number of oblong lignified cells, which gives the phloroglucinol reaction. The presence of *Myristica argentea* in powdered nutmeg may be shown by allowing concentrated sulphuric acid to flow into the sample. The secretion cells of Papua nutmeg show a carmine-red colour, and the rest of the parenchyma a dark yellowish-red, both colours mingling to give a blood red which lasts for some hours. The substitution of *Myristica argentea* may be shown by treating an alcoholic extract with 3 parts of water and 1 part of sodium hydroxide, ammonia, or baryta. Papua nutmeg gives only a yellowish-white colour, while Banda nutmeg (*M. fragrans*) gives a strong reddish-yellow colour (R. Westling, Svensk Farm. Tidskr. 1929, 33, 265).

**Standards.**—The United States standards for nutmeg are as follows: The fixed ether extract shall not be less than 25%, the ash not greater than 5%, the ash insoluble in hydrochloric acid not greater than 0.5%, and the crude fibre not over 10%.

T. McL.

**NUTMEG BUTTER** (*v. MYRISTICA* FATS, this Vol., p. 259 $a$ ).

**NUTMEGS, ESSENTIAL OIL OF.** The oil distilled from the fruits of *Myristica fragrans* Houtt., Fam. Myristicaceae. Nutmegs are cultivated principally in the Moluccas but the tree grows in Penang, Sumatra, Singapore, Ceylon, and the West Indies, and has been introduced into Madagascar, Bourbon, and the Seychelles. Nutmegs yield from 7 to 12% of essential oil.

**Constituents.**—The oil consists largely of terpenes. Pinene, camphene, and dipentene occur to the extent of about 60%, together with terpineol, borneol, and geraniol, with traces of eugenol and isoeugenol, safrole, and myristic acid. *Myristicin*, 3-methoxy-4:5-methylenedioxyallylbenzene, m.p. 36°, is converted by alkali into the propenyl compound, *isomyristicin*, m.p. 45°.

**Characters.**— $\rho_{15.5}^{15.5}$  0.865–0.925,  $\alpha_D^{20}$  +10° to +45°,  $n_D^{20}$  1.474–1.488. Soluble in 3 volumes 90% alcohol. Residue on rapid evaporation in a flat dish not more than 3%.

Oil of nutmegs is mostly used as a flavouring agent, and medicinally in liniments and hair lotions as a mild irritant.

C. T. B.

**NUTRILITE** is a term coined by R. J. Williams (Science, 1928, 67, 607) to include organic substances which in minute amounts



function in the nutrition of organisms of different types. Its meaning is similar to that of vitamin, except that the term vitamin is usually restricted to substances which are effective for animals.

R. J. W.

**NUX VOMICA.** (*Noix vomique*, Fr.; *Krahenaugen*, *Brechnuss*, Ger.) *Strychnos nux vomica* Linn. is a medium-sized deciduous tree which is found throughout south-eastern Asia and in northern Australia. The fruits are about the size, shape, and colour of a small orange, and contain four or five hard and bitter seeds, which constitute the nux vomica of commerce. The diameter of the seeds is usually 15-25 mm. and the thickness varies from 3 to 6 mm.; their shape is circular plano-convex and their colour greenish-grey with a satiny lustre due to a closely appressed covering of fine hairs. They were introduced into Europe during the sixteenth century and have gradually become an important article of *materia medica*.

As a rule nux vomica is obtained from wild trees only. The principal countries of origin are India and Indo-China. During 1925-33 the average exports from Indo-China were about 500 tons per annum (Chemist and Druggist, 1935, i, 77; 1938, ii, 137), while in the period 1933-36 India exported an average yearly quantity of 2,400 tons (*ibid.* 1937, ii, 21). The amount of nux vomica collected in India is greater than the export figures would indicate, for India is herself a considerable producer of strychnine (Pharm. J. 1938, [i], 266, 450).

Although nux vomica is the only important source of strychnine, small quantities of "Ignatius Beans" derived from *S. Ignatii* Berg., a climbing plant of the Philippines, are occasionally offered on the market. The seeds of both these plants contain brucine as well as strychnine, as also do the seeds or other plant parts of many other species of *Strychnos*. Such are, e.g. *S. colubrina* (Greenish, Pharm. J. 1879, [iii], 9, 1014); *S. cinnamomifolia* (Short, Year Book of Pharmacy, 1924, 646); and *S. Ticuti*, which is the "deadly upas tree" of Java. *S. ligustrina*, however, was found to contain brucine only (Greenish, *l.c.*), and *S. Blanda* contained neither alkaloid (Small, Pharm. J. 1915, [iv], 36, 510, 522). Certain poisonous species of *Strychnos* depend mainly upon curarine for their activity.

For further particulars regarding nux vomica, see Oberlin and Schlagdenhauffen (J. Pharm. Chim. 1878, [iv], 28, 225); Dunstan and Short (Pharm. J. 1883, [iii], 13, 1053; 1885, [iii], 15, 1, 1560); Rosell (Monatsh. 1884, 5, 94); Greenish (Pharm. J., 1885, [iii], 15, 60); Ford, Ho Kai, and Crow (*ibid.* 1887, [iii], 17, 927); Flück, a. Hanb. 428; Benth. a. Trim., 178.

The seeds of certain *Strychnos* species, containing less strychnine, resemble nux vomica so closely that occasional adulteration originating with the native collectors is almost inevitable. This has led at times to complaints that Indian seeds contained less strychnine than before (Puntambekar and Krishna, Year Book Pharm. 1932, 633). The same difficulty was encountered when an attempt was made to establish a Siamese export (Pharm. J. 1936, [iv], 83, 38).

The total alkaloid content of nux vomica may vary from 1 to 5%, but the usual sample contains 2.2-2.8%. The corresponding figures for Ignatius beans are 2-3%, of which 60-75% may be strychnine. According to Beckurts (*ibid.* 1889, 20, 341) and Morrison and Bliss (J. Amer. Pharm. Assoc. 1932, 21, 648, 753), roughly 40-45% of the total alkaloids in nux vomica consists of strychnine. Small (Pharm. J. 1913, 90, 510) maintained that strychnine was concentrated mainly in the interior of the seed and brucine mainly in the outer layers, but Puntambekar and Krishna (*l.c.*) could not confirm this. Similarly le Coultre and Van der Wielen (Pharm. Weekblad, 1938, 75, 1329) could not verify the statement of Rosenthaler and Weber (Ber. Pharm. Ges. 1921, 31, 396) that the smallest seeds had the highest alkaloidal content.

The official requirements for the strychnine content of nux vomica and its preparations in Britain and the U.S.A. are as follows: Nux vomica seeds and powder 1.2% (U.S. 1-15%); Tincture of nux vomica 0.125% w/v (U.S. 0.105-0.125%); Extract of nux vomica 5%; Fluid extract 1.5% w/v. The extracts are not official in the U.S.P.

For details of the methods by which strychnine is determined reference should be made to the respective Pharmacopœias. In the British process the mixed alkaloids are liberated by ammonia and extracted with alcoholic chloroform. After a procedure designed to purify the alkaloids from extraneous matter, the mixture of brucine and strychnine is treated with cold dilute sulphuric acid containing some nitric acid. Under the conditions adopted all the brucine is destroyed, while the more stable strychnine is not affected. Excess sodium hydroxide is now added and the base is transferred to chloroform. After removing the solvent the residue is titrated with 0.1N. sulphuric acid.

Allen and Allport (Year Book of Pharm. 1910, 252; cf. *ibid.* 1912, 245) describe a colorimetric process based on the colour test of Malaquin as modified by Denigès (Bull. Soc. chim. 1911, [iv], 9, 537). The assay occupies much less time than that of the B.P., and, though not so accurate, is stated to be sufficiently so for routine work. The total alkaloid in the powdered seeds is liberated by piperazine and extracted with boiling tetrachloroethylene. Transfer is made to dilute sulphuric acid and the strychnine is precipitated as the sparingly soluble ferrocyanide. The precipitate is reduced with dilute hydrochloric acid and zinc amalgam, and sodium nitrite is added. A portion of the reddish liquid is matched in a tintometer and the value of the red component is correlated with the quantity of strychnine present as given in a table.

Dunstan and Short were the first to employ the properties of the hydroferrocyanides in the separation and estimation of strychnine and brucine. The method was elaborated by Beckurts (Arch. Pharm. 1890, 228, 347) and Gadreau (J. Pharm. chim. 1927, [viii], 6, 145) among others. Cumming and Brown (J.S.C.I. 1928, 47, 547r) regarded the separation as approximate only, but Kolthoff and Lingane (J. Amer. Pharm. Assoc. 1934, 23, 302) considered it was accurate if suitable precautions were taken.



Strychnine,  $C_{21}H_{22}O_4N_2$ , was isolated from *nux vomica* seeds in 1818 by Pelletier and Caventou (Ann. Chim. Phys. 1818, [ii], 10, 14; 1823, [ii], 26, 44). That strychnine is also present in the bark was shown by Shenstone (Pharm. J. 1878, [iii], 8, 445; 9, 154).

**Preparation.**—The following process may be used for the extraction of brucine and strychnine from the finely powdered seeds of *S. nux vomica*. The powder is made into a paste with water and one-fourth its weight of slaked lime. The mixture is thoroughly dried on the water-bath and the mass is powdered. The alkaloids are now dissolved from it by hot percolation with a suitable solvent, such as chloroform, in an extraction apparatus. The solvent is shaken out with sulphuric acid and the sulphates are crystallised. Alternatively the alkaloids may be regenerated and extracted with 25% alcohol, or with acetone, which dissolves the brucine and leaves behind most of the strychnine.

*Nux vomica* seeds are very tough, and on the large scale they are sometimes steamed, or autoclaved with water, to soften them before disintegration. Descriptions of industrial processes, which do not differ greatly from the above, are given by Chemnitz (Chem.-Ztg. 1926, 50, 845), and by Watson and Sen (Quart. J. Indian Chem. Soc. 1926, 3, 397).

**Properties.**—Strychnine forms rhombic prisms, m.p.  $268^\circ$ , and distils without decomposition at  $270^\circ/5$  mm. (Loebisch and Schoop, Monatsh. 1886, 6, 858). Warnat (Helv. Chim. Acta, 1931, 14, 997) gives the m.p. as  $286-288^\circ$  and  $[\alpha]_D -110^\circ$  in 80% alcohol and  $-139.3^\circ$  in chloroform. Very slightly soluble in water (1 in 6,667 at  $15^\circ$ ; 1 in 2,500 at  $100^\circ$ ), giving an alkaline solution the bitterness of which is still perceptible on dilution to 1 in 700,000. Solubility in 90% alcohol 1 in 170 (cold), 1 in 12 (boiling); ether 1 in 5,500; chloroform 1 in 6; benzene 1 in 150; amyl alcohol 1 in 180.

Strychnine is a moderately strong monoacidic base. The hydrochloride,  $B \cdot HCl \cdot 2H_2O$ , which is official in the British Pharmacopoeia, forms prisms soluble in 35 parts cold water and 73 parts 90% alcohol. On the continent, and in Japan, the nitrate,  $B \cdot HNO_3$ , is largely used; this crystallises in needles soluble in 80 parts water at  $18^\circ$ , in 45 parts at  $25^\circ$ , and in 45 parts alcohol. In the U.S.A. both the nitrate and the sulphate,  $B_2 \cdot H_2SO_4 \cdot 5H_2O$ , are employed; the latter salt forms prisms soluble in 31 parts water at  $25^\circ$ , and in 125 parts alcohol. Of the other salts the hydroferrocyanide, chromate, thiocyanate, and hydroiodide are sparingly soluble. Strychnine picrate, m.p.  $270^\circ$ , forms greenish-yellow rosettes, the individual crystals of which are often curved in a characteristic manner (Nelson and Leonard, J. Amer. Chem. Soc. 1922, 44, 369). It is stated to be much less soluble in acetone than the picrates of most other alkaloids.

**Uses.**—Strychnine is employed as a bitter tonic and as a heart stimulant, the usual dose being 1-4 mg. As little as 32 mg. has been known to cause death. In poisonous doses it gives rise to tetanic spasms, owing to the greatly increased excitability of the spinal cord, and death eventually supervenes through failure of respiration. More than half the world's produc-

tion is used for killing vermin, especially rabbits, rats, and gophers. In this country, however, its employment for this purpose is restricted to the killing of moles, under certain conditions.

**Reactions and Detection.**—Strychnine, which is one of the most stable alkaloids, is not coloured or decomposed by sulphuric acid at  $100^\circ$ . This property is made use of in toxicology, to free the alkaloid from extraneous impurities. It dissolves in nitric acid, giving at most a yellow colour. A striking colour reaction was described by Marchand (J. Pharm. chim. 1843, [iii], 4, 200). In this test a small quantity of the alkaloid is dissolved in a few drops of concentrated sulphuric acid, and a minute fragment of potassium dichromate or other oxidising agent is stirred in. A play of colours is observed, beginning with blue and passing through violet and red to yellow. Only curarine behaves exactly like strychnine, and this is coloured blue by sulphuric acid alone. To prevent the colours being obscured the alkaloid must first be isolated in as pure a state as possible. In particular brucine, which gives a deep red colour when oxidised, must be completely removed if present. This alkaloid may, however, be selectively oxidised with nitric acid, the strychnine being recovered (Shenstone, l.c.; Hanriot, Compt. rend. 1883, 97, 267; Gerock, Arch. Pharm. 1889, 227, 158); or the mixed alkaloids may be washed with chlorine water, when dichlorobrucine is formed and dissolves, leaving a residue of strychnine (Beckurts, *ibid.* 1890, 228, 326).

Brucine,  $C_{25}H_{26}O_4N_2$ , was isolated from *nux vomica* bark and seeds in 1819 by Pelletier and Caventou (Ann. Chim. Phys. 1819, [ii], 12, 118; 1823, [ii], 26, 53). Usually about 55-60% of the alkaloids present in the seeds consists of brucine. The alkaloid contained in the bark may reach 7-8%, and is almost entirely brucine.

**Preparation.**—The total alkaloid having been extracted by the method described for strychnine, the mixture is repeatedly washed with 25% alcohol, and the brucine is crystallised from the solution and recrystallised several times from the same solvent, the fractions which crystallise latest being pure brucine. Alternatively the mother-liquids from strychnine may be concentrated and the alkaloids precipitated as neutral oxalates. The precipitate is dried and extracted with absolute alcohol, in which the strychnine salt is the more soluble. The alkaloid from the residue is regenerated and purified as sulphate. According to Flückiger, if the mixed alkaloids are converted to acetate, and the solution is evaporated to dryness on the water-bath, the strychnine salt dissociates and acetic acid volatilises. The brucine acetate is unchanged and may be dissolved from the residue by cold water.

**Properties.**—Brucine separates from its solutions in water or weak alcohol in monoclinic prisms containing  $4H_2O$ , m.p.  $105^\circ$ , or with  $2H_2O$  from alcohol (Moufang and Tafel, Annalen, 1889, 304, 24). The crystals lose their water at  $100^\circ$ , or on standing over sulphuric acid, and the anhydrous substance melts at  $178^\circ$  (Claus, Ber. 1881, 14, 773). It has  $[\alpha]_D -85^\circ$  in alcohol,  $-120^\circ$  in chloroform (Oude-

mans, Annalen, 1873, 166, 69). Solubility in water 1 in 320 (cold), 1 in 150 (boiling). In alcohol it is soluble to the extent of 1 in 2.2 at 25°, in chloroform 1 in 8.7 at 25°, and in ether 1 in 133. Brucine and its salts are bitter and when injected subcutaneously into animals produce a physiological action similar to that of strychnine but much feebler. Internal administration produces little effect, owing chiefly to the rapidity of elimination (Brunton, J.C.S. 1885, 47, 143). Brucine is a monoacidic tertiary base; the sulphate,  $B_2 \cdot H_2SO_4 \cdot 7H_2O$ , crystallises in long needles and like most of the other salts is more soluble than the corresponding salt of strychnine. The hydriodide is, however, less soluble than the strychnine compound (Shenstone, *ibid.* 1881, 39, 456).

**Reactions and Detection.**—Brucine, unlike strychnine, does not give rise to a play of colours when oxidised with chromic acid, etc., only an intense red coloration being produced. A deep red colour is also obtained on dissolving brucine in nitric acid, or, better, on dropping nitric acid into a solution of brucine in sulphuric acid; this is a very delicate test both for brucine and nitric acid. The coloration may be distinguished from that produced when certain other alkaloids are treated with nitric acid by the action of stannous chloride or other reducing agent, which, when cautiously added, changes the colour to violet (Wober, Z. angew. Chem. 1918, 31, 124).

**Uses.**—In the U.S.A. brucine is used to denature industrial alcohol, but so far as Britain is concerned its employment in this manner is confined to surgical spirit, which may contain not more than 0.015% of brucine [Poisons (Amendment) Rules, 1912].

**Minor Constituents of Nux Vomica.**—Dunstan and Short (Pharm. J. 1881, [iii], 14, 1025) isolated a glucoside, m.p. 215°, from the seeds and fruit-pulp of nux vomica, and named it "loganin." This was found by Rosenthaler (Sweiz. Apoth. Ztg. 1923, 339) to be a mixture, of which the principal constituent was identical with the glucoside *meliatin* extracted by Bridel (Compt. rend. 1911, 152, 1691) from the marsh trefoil. Bridel gave in p. 222°,  $[\alpha]_D - 82^\circ$  (water) for the pure substance, and, following his suggestion (Bull. Soc. Chim. biol. 1923, 5, 800), the name "loganin" has now been supplanted by *meliatin*. The "igauric acid" of Pelletier and Caventou (Ann. Chim. [ii], 10, 167; 26, 54) was further discussed by Ludwig (Arch. Pharm. 1856; [iii], 2, 137), Corriol (J. Pharm.

chim. 1833, 19, 155), Marsson (Annalen, 1849, 72, 296), Sander (Arch. Pharm. 1897, 235, 133). According to Gorter (*ibid.* 1909, 247, 197) and Tunmann (Pharm. Post. 1918, 341) it is identical with *chlorogenic acid* from coffee berries, i.e., with 3-[3:4-dihydroxyeinnaoyl]-1-quinic acid. Other constituents are 11% proteins, mucilage, sugar, and about 4% of a fatty oil. See Meyer (J.C.S. 1875, 28, 856); Greenish (Pharm. J. 1882, [iii], 12, 581); Harvey and Wilkes (J.S.C.I. 1905, 24, 718); Watt and Angus (*ibid.* 1916, 35, 201).

See also STRYCHNOS ALKALOIDS.

R. G. J. and H. E. W.

## NYCTANTHES ARBOR-TRISTIS

Linn., a large shrub with rough leaves and sweet-scented flowers, occurs in the sub-Himalayan and Tarai tracts, and also in Central India, Burma, and Ceylon. The orange corolla tubes of the flowers give a beautiful but fleeting dye which is mostly used for silk, sometimes in conjunction with safflower or turmeric, occasionally with indigo and kath (v. Vol. II, 433c). The bark of the tree is said to be employed for tanning; the leaves appear to be used medicinally (Watt, "Dictionary of the Economic Products of India," 1891, 5, 434).

From an aqueous extract of the flowers, Hill and Sirkar (J.C.S. 1907, 91, 1501) isolated mannitol and a red colouring matter, *nyctanthin*, which Perkin (*ibid.* 1912, 101, 1539) showed was identical with the colouring matter obtained from the flowers of the *Cedrela Toona* Roxb. Subsequently, Kuhn and Winterstein (Helv. Chim. Acta. 1929, 12, 496) established that nyctanthin is identical with crocetin (v. Vol. III, 428c; Vol. II, 440a).

From the leaves Lal and Dutt (Bull. Acad. Sci. Agra and Oudh, 1933, 3, 83) obtained mannitol, a resin, a glucoside, m.p. 71°, glucose and a trace of essential oil, but no alkaloid could be detected. The results of a chemical examination of the fixed oil from the seeds of *Nyctanthes arbor-tristis* are recorded by Varistha (J. Benares Hindu Univ. 1938, 2, 343).

For dyeing purposes the material (silk or cotton) is simply steeped in a hot or cold decoction of the flowers. The addition of alum and lime juice to the dye-bath is said to render the colour more permanent.

E. J. C.

NYCTANTHIN (v. Vol. II, 439d).

NYLON (v. Vol. IV, 125d; V, 112b, 113b, 126a).

## O

OATS (v. Vol. II, 489b).

OBERMÜLLER TEST (v. Vol. IV, 547d).

OBTUSATIC ACID (v. Vol. VII, 296d).

**OCHRE.** The majority of natural mineral pigments, of which ochres are the most important, owe their colour to iron in the form of the hydrous oxide, "limonite," or the anhydrous ferric oxide, hematite, and to a lesser extent to oxides of manganese. Yellow ochre, the commonest natural pigment, consists of yellowish-

brown limonite together with varying amounts of clay, siliceous matter, and other impurities. The iron oxide content varies from 15 to 30% or more. It is known by many names, including Mineral Yellow, Permanent Yellow, Roman Earth or Ochre, Chinese Ochre, etc. The best varieties are lemon-yellow to golden-yellow. With increasing iron the colours usually shade towards yellow-brown (sienna), though no sharp division exists between ochre and sienna in either colour or iron content. The value of

an ochre depends more upon its physical properties than upon its content of ferric oxide, and is also dependent upon its degree of oil absorption. Sometimes the crude ochre can be used after having been simply dried and ground, but a certain amount of washing is usually desirable before drying and pulverisation. When roasted the yellow ochres yield reddish-brown colours (burnt ochre), due to the conversion of limonite to the red ferric oxide, hematite. *Red ochre* is a natural pigment resembling burnt ochre, its colour being due to the presence of abundant hematite. The name *golden ochre* is applied to both the natural golden-yellow ochre and to yellow ochre that has been toned with up to 15% of chrome yellow. *Green ochre*, also called green earth, terre verte, Celadon green, etc., is the only important natural mineral green. It is a low-tinting pigment used widely as a base for cheap lakes, and consists largely of ferro-magnesian silicate minerals such as chlorite. *Umbre* is an ochre containing manganese oxides ( $\text{MnO}_2$  7-23 and  $\text{Fe}_2\text{O}_3$  25-50%) and often organic matter. It has a darker shade of brown than sienna, and when roasted it is converted to a deep red burnt umbre.

Ochres are of widespread occurrence, though individual deposits are usually small and of sporadic distribution. The deposits result from the prolonged weathering of ferruginous rocks, which may have originally contained only a small proportion of iron. Some iron ores serve as red or brown mineral pigments. Many ochreous deposits occur in rock cavities and fractures, or accumulate in old mine workings, the iron having been leached out of the surrounding rocks by percolating waters, especially when iron pyrites is present. The annual world production of ochres and umbers probably exceeds 100,000 tons.

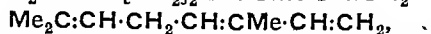
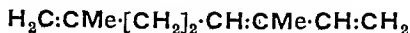
Ochres are used extensively as protective paints on steel and ironwork. Low-grade varieties serve as combined pigments and fillers in the manufacture of linoleum, oilcloth, and inferior mixed paints, whereas high-grade ochres are employed in making superior mixed and paste-paints, and occasionally in the preparation of artists' colours. Some of the best yellow ochres are obtained from France.

In mineralogy the term "ochre" is also applied to numerous earthy metallic oxides resulting from the decomposition of metallic minerals, e.g., antimony-ochre, bismuth-ochre, vanadic-ochre, and wolfram-ochre.

*References.*—R. B. Ladoo, "Non-Metallic Minerals," New York, 1925, p. 368 (comprehensive); H. Wilson, in "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, New York, 1937, Chap. XXVIII (good bibliography); S. J. Johnstone, "Minerals for the Paint Industry," J. Oil and Colour Chemists Assoc., 1941, 24, 263; R. W. Pocock, "Ochres, Umbers, and other Natural Earth Pigments of England and Wales," Geol. Survey Great Britain, 1942, Wartime Pamphlet No. 21.

D. W.

## OCIMENE,



b.p. 81/30 mm.  $\rho^{15}_D$  0.8031,  $n^{15}_D$  1.4857 occurs in a number of essential oils, *inter alia* those from

the leaves of *Ocimum basilicum* Linn., *O. gratissimum* Linn., and *Honoranthus flavescescens* (v. TERPENES).

J. L. S.

**OCTANE NUMBER.** Octane number is a unit commonly used as a measure of the tendency of a fuel to cause detonation (pinking or knocking) in spark-ignition engines. It is numerically equal to the percentage by volume of 2:2:4-trimethylpentane (*isooctane*) which must be blended with *n*-heptane to give a blend having the same tendency to detonation (antiknock value) as the test fuel under specified conditions in a test engine. The octane number is one of the most important properties of a fuel intended for use in spark-ignition engines, as will appear in the sequel.

**Detonation.**—In a spark-ignition engine a mixture of air with atomised and partly vaporised fuel is admitted to each cylinder and is compressed by the movement of the piston during the compression stroke. The mixture is then ignited by the passage of an electric spark across the terminals of the spark plug. Owing to the heat evolved by the strongly exothermic combustion reaction, and, to a lesser extent, to the increase in the number of molecules, the combustion results in a considerable increase of pressure in the combustion space of the engine, the pressure rise providing the power which drives the engine.

The flame starts at the spark plug and, in normal non-detonating combustion, travels smoothly across the combustion space at a speed of the order of 50-100 ft. per second. Owing to the pressure rise incident on combustion, the unburnt fuel-air mixture ahead of the flame is progressively compressed and its temperature therefore increases. When the fuel and engine operating conditions are such that detonation occurs, the unburnt fuel-air mixture ahead of the flame suddenly ignites spontaneously, and the remainder of the mixture burns at a much greater rate than in normal combustion. Rassweiler and Withrow have demonstrated this very clearly by taking high-speed photographs of the flame in an engine fitted with a transparent quartz window in the cylinder head (Trans. Soc. Aut. Eng. 1936, 31, 297). This spontaneous ignition causes a sudden increase in pressure, gas vibrations, and impacts on the walls of the combustion chamber, which give rise to the characteristic "metallic" noise associated with detonation (*idem*, Aut. Eng. 1934, 24, 281, 385).

Detonation must be carefully distinguished from pre-ignition, which is due to the ignition of the mixture by incandescent carbon deposits, overheated spark-plug points, etc. Pre-ignition occurs *before*, detonation *after* passage of the spark. Of two fuels, A and B, A may have the better detonation, B the better pre-ignition characteristics.

The occurrence or non-occurrence of detonation depends on the characteristics of the fuel and on the design and operating conditions of the engine. The engine and operating factors affecting detonation are compression ratio, degree of supercharging, spark advance, mixture strength, speed, mixture temperature, cylinder

temperature, shape and physical dimensions of the combustion chamber, design of valves and valve ports (which affect swirl or turbulence of the mixture), amount of oil burned, etc. Increase of compression ratio, greater supercharging and advance of spark all increase the tendency to detonation. Detonation is a maximum at a mixture strength some 15–20% greater than that indicated by the chemical equation for complete combustion.

At the end of the compression stroke the mixture reaches a pressure of the order of 10–15 atmospheres and a temperature of the order of 300–400°C., depending on the engine and operating conditions. Even before the passage

of the spark appreciable oxidation of the fuel can occur. By cooling the exhaust gases from an engine motored, without sparking, Peletier, Van Hoogstraten, Smittenberg, and Kooyman obtained, in addition to unchanged fuel, an aqueous liquid containing 30% by wt. of peroxides; addition of this liquid to the fuel charge to an engine operating near the detonation limit caused violent detonation (Chaleur et Ind. 1939, 20, 120).

Withrow, Lovell, and Boyd determined the oxygen content of gas samples taken from different points in the combustion chamber and at various times during the working stroke, and thus showed that a comparatively narrow band

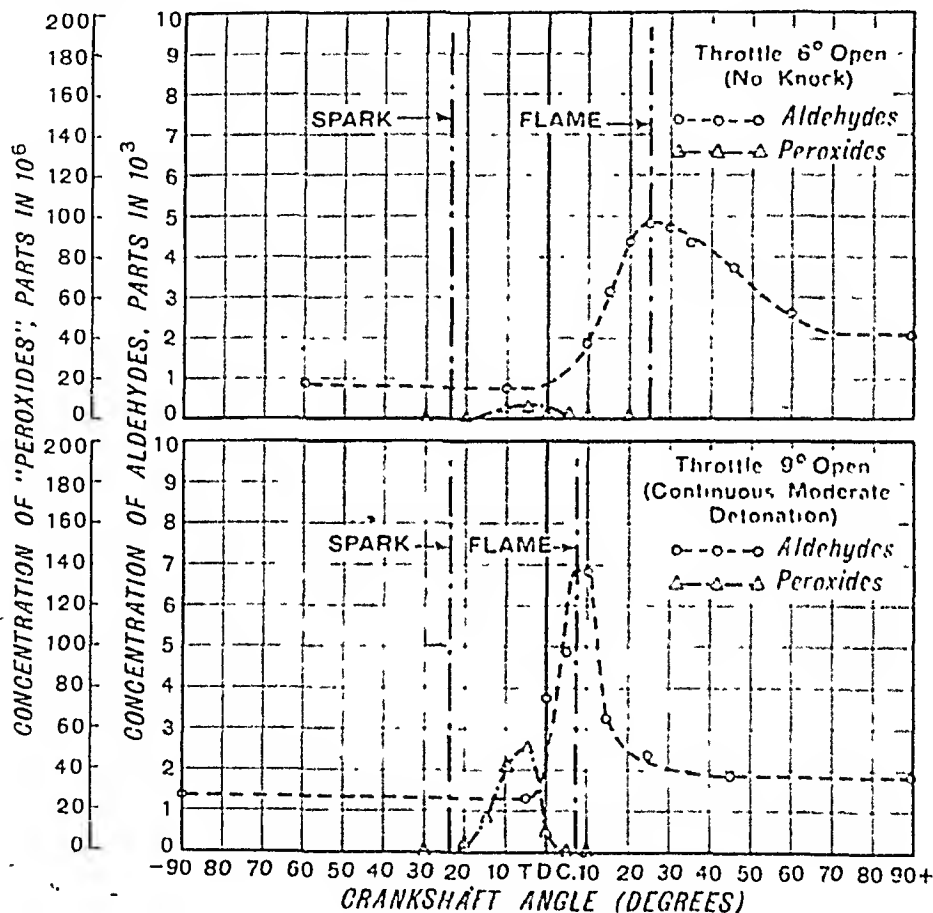


FIG. 1.

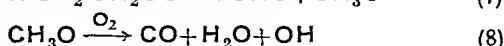
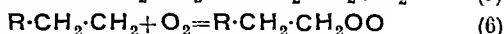
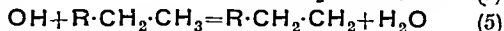
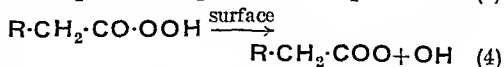
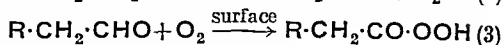
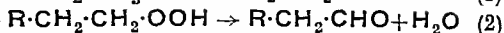
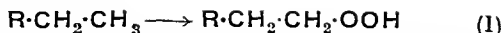
of combustion travels outward from the spark plug and that combustion is practically completed in this narrow zone (Ind. Eng. Chem. 1930, 22, 945). Chemical analysis and spectroscopic observations of engine flames through a quartz "window" have also shown that formaldehyde is always present in the unburnt gas which is about to knock (Withrow and Rassweiler, *ibid.* 1934, 26, 1256; Egerton, Smith, and Ubbelohde, Phil. Trans. 1935, A, 234, 433; Ubbelohde, Drinkwater, and Egerton, Proc. Roy. Soc. 1935, A, 153, 103). Egerton *et al.* (*l.c.*) also showed that the maximum concentrations of aldehydes, and especially of peroxides, are greater in knocking than in normal combustion, typical results being given in Fig. 1 (T.D.C.=top dead centre, *i.e.*, the

position of the piston at the point of maximum compression). The line marked "Flame" indicates the position of the piston when the flame reached the sampling valve. The peroxides consisted mainly of nitrogen peroxide, but small quantities of organic peroxides, behaving like ethyl hydrogen peroxide, were also detected.

The oxidation of hydrocarbon fuels in an engine cylinder undoubtedly occurs by a chain-reaction mechanism, which is characterised by an induction period followed by a rapidly increasing reaction rate; in the later stages the rate decreases as the reactants are consumed (*cf.* Pease, J. Amer. Chem. Soc. 1929, 51, 1839). Although the temperature and pressure at the end of the compression stroke lie well within the

ignition regions of hydrocarbons, the time available (of the order of 0.015 second) is normally less than the ignition lag (induction period), so that, in the absence of "hot spots" (pre-ignition), true combustion is initiated by the spark. In the unburnt gas ahead of the flame, however, the temperature and pressure may rise to over 700°C. and 30 atm. respectively, under which conditions the ignition lags are much shorter, and it is possible for spontaneous ignition and detonation to occur.

The main sequence of reactions involved in the oxidation of paraffin hydrocarbons in an engine is probably as follows, though chain branching can occur (adapted from von Elbe and Lewis, *Ind. Eng. Chem.* 1937, 29, 551):



$R\cdot CHO$  formed in (7) can then go through the series of reactions starting at (3), and so on.

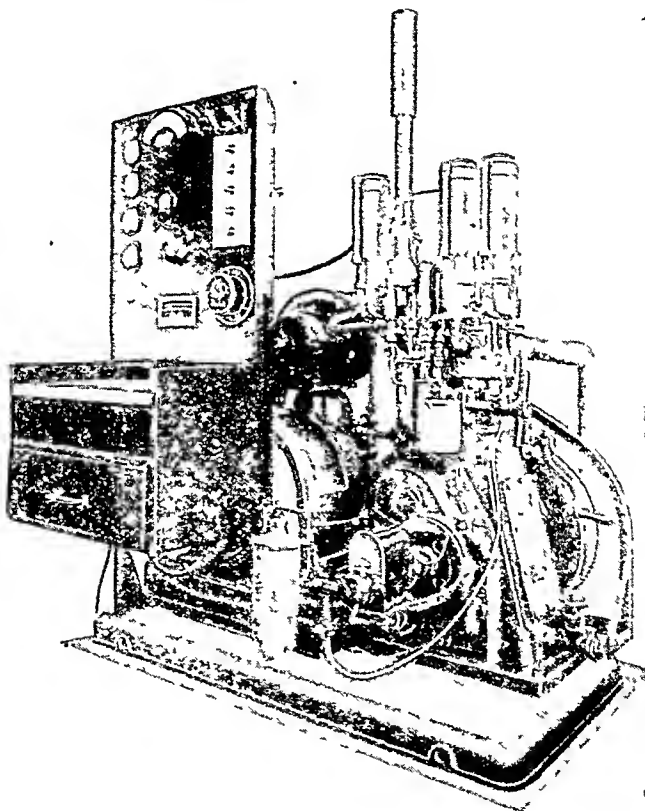


FIG. 2.

With isomeric paraffins, oxidation starts at the end of the longest alkyl group.

The oxidation of higher olefins in an engine follows a course similar to that of the higher paraffins, starting at the end of the molecule and not at the double bond. In the case of the lower aromatics, the mechanism is less well established.

**Measurement of Octane Number.**—Early attempts at measuring the antiknock values of fuels were made using existing single or even multi-cylinder engines, fuels being compared on the basis of the spark advance or

throttle opening required to give the same degree of detonation. One of the first engines specifically designed for the purpose was the R.35 engine (Ricardo, *Aut. Eng.* 1921, 11, 51, 92, 130). In this engine the compression ratio could be varied within wide limits during operation by raising or lowering the cylinder relative to the rest of the engine. The compression ratio at which a specified degree of slight detonation was obtained under standardised operating conditions was called the H.U.C.R. (highest useful compression ratio) of the test fuel.

Midgley devised a knock indicator known as the "bouncing pin" (J. Soc. Aut. Eng. 1922, 10, 7) which provided a means of measuring detonation intensity in place of its estimation by the ear. A modified form (*see below*) is at present widely used.

It was obviously necessary to have a uniform, reproducible and generally accepted procedure for determining the knock characteristics of fuels and in 1928 a sub-committee of the C.F.R. (Co-operative Fuel Research) Committee was formed in the U.S.A. to develop a suitable engine

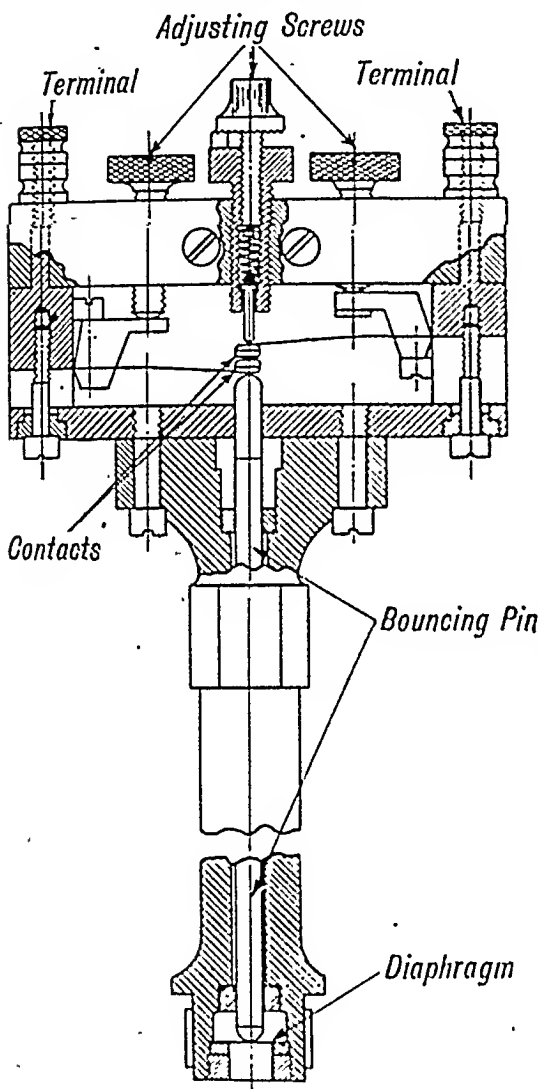


FIG. 3.

and procedure. The engine now used (Fig. 2) is a 4-stroke engine, the compression ratio of which is infinitely variable during operation between 3:1 and 30:1, the normal working range being from 4:1 to 10:1. It is liquid cooled, to facilitate accurate control of cylinder temperature. The spark advance is automatically varied with the compression ratio, and means are provided for indicating the spark advance while the engine is running. The carburettor is provided with three float bowls, which can be raised or lowered to permit accurate adjustment of mixture strength; the multiple float-bowl

design facilitates the rapid change-over from test fuel to reference fuels and *vice versa*.

Intensity of detonation is measured with the aid of a bouncing pin (Fig. 3). This instrument is screwed into the cylinder head approximately at the point where detonation occurs. The terminals are connected to an electric circuit comprising a resistance heating-coil located near a thermocouple; thus the potential produced by the thermocouple depends on the period of time that the bouncing-pin contacts are closed. The tensions of the leaf springs on which the contacts are mounted are adjusted so that the circuit is not closed by impulses caused by normal combustion pressures. When detonation occurs, the resulting rapid increase in cylinder pressure throws the bouncing pin off the thin steel diaphragm and closes the circuit for a period of time depending on the intensity of detonation. The potential produced by the thermocouple is measured on a millivoltmeter, which is called a knockmeter and is calibrated from 0 to 100.

Briefly, the octane number test is carried out by adjusting the compression ratio to give a specified knockmeter reading (intensity of detonation) with the test fuel, and bracketing the latter, on the basis of knockmeter readings, between reference-fuel blends, one blend being slightly higher and the other slightly lower in antiknock value than the test fuel. The primary reference fuels are pure isooctane (2:2:4-trimethylpentane) and pure n-heptane. Tests are normally made against secondary reference fuels such as technical isooctane and various stable gasolines, with or without addition of Ethyl fluid, the results being converted to octane numbers by use of an established conversion table or chart. The engine operating conditions were chosen to give the best correlation with the antiknock performance of fuels in cars on the road and the method is therefore sometimes known as the "Motor Method." The more important conditions are summarised in Table I.

TABLE I.—PRINCIPAL CONDITIONS FOR KNOCK-RATING TEST METHODS.

	Method.		
	Motor.	Research.	1-C (F-3).
Speed, r.p.m.	900	600	1,200
Jacket temp., °F.	212	212	374
Spark advance, degrees	Automatically varied.	13	35
Intake air temp., °F.	Room.	125	125
Mixture temp., °F.	300	No heat applied.	220
Mixture strength	For max. knock.	For max. knock.	For max. thermal plug temp.

This method has been adopted as standard by the Institute of Petroleum and by the American Society for Testing Materials (A.S.T.M.). Another method, the A.S.T.M. Research Method, employs somewhat milder conditions. It is intended purely for research purposes, the difference between the Research and Motor

Method octane numbers giving a rough estimate of the sensitivity of fuels to changes in engine conditions. The Research and Motor Method octane numbers of paraffins do not usually differ by more than a few units; for olefins and aromatics, however, the Research Method usually gives distinctly higher results, while the few available results on *cycloparaffins* do not permit generalisation. A third method, the 1-C (see Table I), now officially designated F-3 in the U.S.A., was developed to correlate with ratings in aircraft engines under weak-mixture cruising conditions. Apart from differences in engine conditions, the 1-C (F-3) method specifies a thermal plug instead of a bouncing pin as a measure of detonation. The thermal plug is, in fact, a thermocouple, so that fuels are compared on the basis of the temperature rise, rather than the rate of pressure increase, incident on detonation. The engines used for all three methods are similar, though not identical.

**Effect of Engine Conditions.**—The order in which fuels are rated depends to a considerable extent on the engine conditions employed. Fundamentally the incidence of detonation depends on the condition (pressure, temperature) of the gaseous fuel-air mixture at the point where detonation occurs. Since reactions involving induction periods are concerned, time is also a factor, and thus engine speed has an important effect. Speed and the design of valves and valve ports also control the degree of turbulence and thus the rapidity of the combustion. In general, an increase in speed raises the knock ratings of paraffins and *cycloparaffins* relative to those of aromatics, though exceptions occur (Lovell, Amer. Petroleum Institute, Second Annual Report, 1st September, 1939, and 31st August, 1940). Fuels differ considerably in regard to the effect of boost pressure (degree of supercharging); the knock ratings of *cycloparaffins*, and to a greater extent of aromatics, usually are higher, in relation to that of 2:2:4-trimethylpentane, the higher the boost pressure, while considerable differences are found between even closely related branched-chain paraffins. Higher engine temperatures, due to increase in jacket or mixture temperatures, normally decrease the knock ratings of aromatics relative to *cycloparaffins* or paraffins.

Mixture strength has an important effect both on the absolute and relative knock ratings of fuels, and this effect is of greater significance in the case of aero-engines than in the case of cars, owing to the difference in the conditions of operation. Quite apart from any limitations due to detonation, increase of mixture strength up to approximately 150% of that indicated by the "chemically correct" mixture results in a considerable increase in power, though at the cost of increased fuel consumption. Rich mixtures are therefore used for take-off, where high power is needed for a short time. On the other hand, for cruising, a low fuel-consumption is required because range of operation and payload are limited by the quantity of fuel carried, and mixtures slightly weaker than the "chemically correct" are used. Thus the antiknock values of aviation fuels of both rich and weak mixtures are of great practical interest.

Fig. 4 shows two typical mixture response curves, that is, curves giving the relation between mixture strength (fuel-air ratio) and the power output as limited by incipient detonation. In testing aviation fuels, the power output is altered by varying the degree of supercharging (boost pressure) at constant compression ratio. Fuels are rated by establishing mixture response curves for the test fuel and for a reference fuel of known rating. It is common practice to plot specific fuel consumption (lb. per h.p.-hr.) instead of fuel-air ratio, as the two are related and this procedure avoids the complication of accurately measuring the air flow through the engine. In the case of rich mixture ratings, the test fuel and reference fuel are compared at the specific fuel consumption corresponding to the maximum point on the mixture response curve of the reference fuel. Thus, if the accepted rich mixture rating of the reference fuel is 100 and the power outputs obtainable with the test and reference fuels are  $x$  and  $y$  respec-

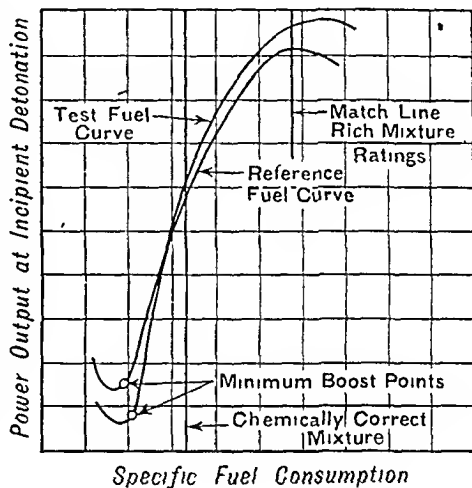


FIG. 4.

tively, the rich mixture rating of the test fuel is  $100(x/y)$ .

Although the 1-C (F-3) rating has been widely used as an indication of weak-mixture performance, this is not necessarily true for all engines and in any case it is necessary to check the degree of correlation between the laboratory ratings and those in full-scale engines. The method adopted for determining the weak-mixture ratings of fuels in full-scale engines is briefly as follows. Referring to Fig. 4 it will be noted that at weak mixtures each curve passes through a minimum. Just on the rich-mixture side of this minimum is a point marked "minimum boost point." This is the point of maximum tendency to detonation; at richer or leaner mixtures, higher boost pressures can be used before detonation is encountered. The shape of the curve on the weak-mixture side of this minimum boost point is due to a compromise between two factors. The slower rate of burning of the weaker mixtures decreases the tendency to detonation and allows higher boost pressures



to be used, while the smaller proportion of fuel in the weaker mixtures tends to reduce the power output. The minimum boost point corresponds approximately to the specific fuel-consumption under economical cruising conditions, *i.e.*, slightly weaker than the "chemically correct" mixture strength. If the weak-mixture rating of the reference fuel is taken as 100 and the minimum boost points of the test and reference fuels occur at boost pressures, in absolute units, of  $p$  and  $q$  respectively, then the weak mixture rating of the test fuel is 100 ( $p/q$ )

The curves in Fig. 4 illustrate the fact that one fuel may be better than another at rich

mixtures, but that the order of rating may be reversed at weak mixtures.

For specifying the antiknock value of aviation fuels, the present trend appears to be towards the use of rich and weak mixture ratings as outlined above, instead of octane number, though the latter unit is still in use. Octane number will probably be used for motor gasolines for some time to come.

**Significance of Antiknock Value.**—So far as motor-car engines are concerned, the antiknock value of the fuel is mainly important in setting a limit to the compression ratio that can be used. As in all thermodynamic cycles,

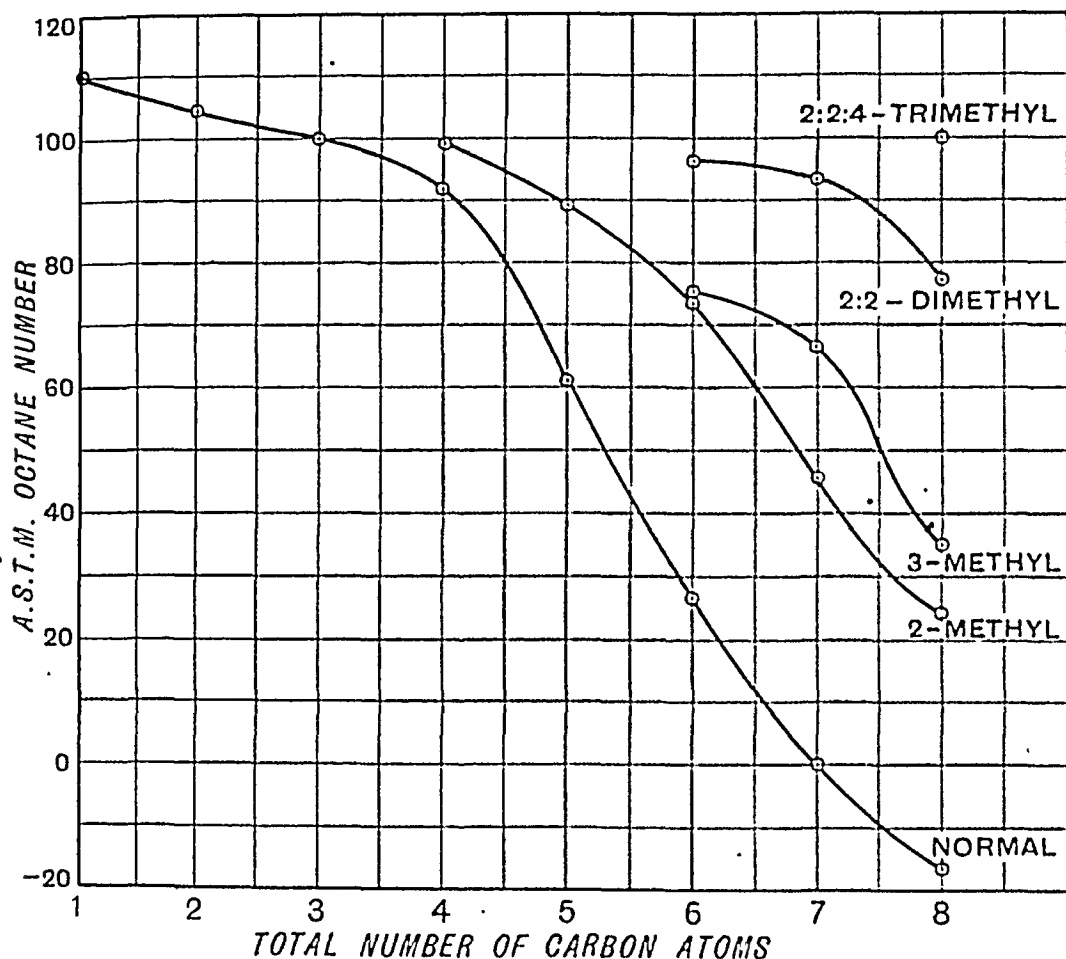


FIG. 5.

higher compression ratios result in greater efficiency and hence increased power and improved acceleration. Knock tests with cars on the road have shown that the A.S.T.M. octane number of a fuel is a good indication of its actual knocking tendency in the average car.

In aero engines, a high antiknock value at rich mixtures is necessary to give the maximum power at take-off. When high power is required, increased supercharging is a more effective method of utilising higher fuel antiknock value than increase of compression ratio, since the former involves charging proportionately greater amounts of fuel and air to the engine. Hence, for take-off, the rich mixture rating provides a more accurate indication of antiknock per-

formance than does the octane number. Under cruising conditions a low fuel consumption is of primary importance, because each pound of fuel carried means one pound less in payload or alternatively for the same payload, a decrease in fuel consumption means an increase in range. With large aeroplanes on long flights, a decrease of 1% in fuel consumption would allow several times that increase in payload, owing to the high ratio of weight of fuel carried to payload. Thermal efficiency is only slightly affected by supercharging, but markedly increases with compression ratio. Thus, for maximum fuel economy under cruising conditions the compression ratio should be as high as possible. In practice some compromise is necessary, to obtain high power

at take-off, because the higher the compression ratio, the lower is the permissible boost pressure before detonation occurs with a given fuel. The 1-C octane number provides a satisfactory indication of antiknock performance under cruising conditions for many aero engines; in other cases the weak-mixture rating based on the minimum boost point is used.

Detonation causes very rapid combustion of part of the combustible mixture in the cylinder and thus tends to reduce the power output, although moderately heavy audible detonation is necessary before this becomes appreciable. In motor-car engines even fairly heavy detona-

tion rarely causes damage to the engine. In aero engines detonation is less easily detected owing to the higher noise level and may result in sticking of the piston rings, pitting and burning of the piston and, in severe cases, wreckage of the engine within a short time.

**Relation between Chemical Structure and Octane Number.**—Octane numbers of various hydrocarbons and of a few alcohols, ketones, and a branched-chain ether are given in Table II, and in Figs. 5 and 6 octane numbers of paraffins and cycloparaffins, respectively, are plotted against the number of carbon atoms.

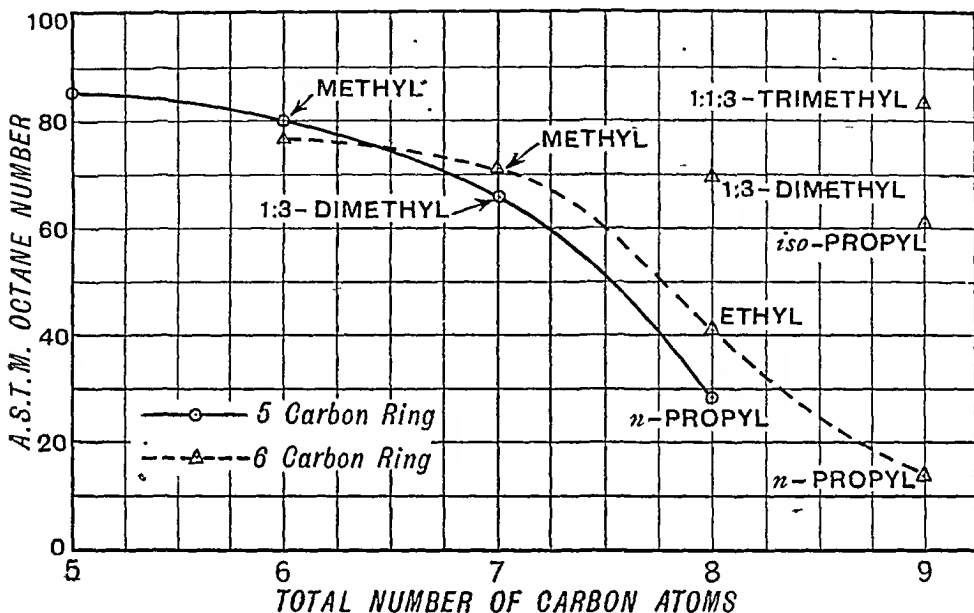


FIG. 6.

Octane number decreases with increase in the number of carbon atoms for hydrocarbons of similar structure (*i.e.*, normal, 2-substituted, 3-substituted paraffins, etc., respectively), ethylene and propylene (81 and 85 octane number respectively) being the only exceptions noted so far. Among paraffins and olefins, the octane number is higher the more compact the molecule (*cf.* Fig. 5). This effect of branching of the hydrocarbon chain in increasing the octane number is in line with the scheme of hydrocarbon oxidation outlined earlier. Equations (3) to (7) indicate that, starting at the end of the longest alkyl group, carbon atoms are progressively removed by oxidation via an aldehyde. When a side chain is present, this process will eventually result in a ketone, which is less easily oxidised than an aldehyde and the oxidation process, and hence detonation, are arrested (Pope, Dykstra, and Edgar, *J. Amer. Chem. Soc.* 1929, 51, 2203). Rice has shown that the knocking tendency of hydrocarbons increases with increase in the number of molecules formed by the thermal decomposition of one molecule of the hydrocarbon (*Ind. Eng. Chem.* 1934, 26, 259).

Comparing paraffins and olefins of similar structure and with the same number of carbon atoms, ethane and propane are superior to ethylene and propylene, but, for the higher members, the olefins have the higher octane numbers, the difference increasing with molecular weight. The position of the double bond in olefins apparently has little effect, as would be expected if oxidation starts at the end of the carbon chain instead of at the double bond (*see above*). Stereoisomers (*e.g.*, *cis*- and *trans*-butene-2) have the same octane numbers.

Cycloparaffins with five or six carbon atoms in the ring exhibit similar relationships to paraffins (Fig. 6). Several methyl groups are more effective than the same number of carbon atoms in a single alkyl group (*cf.* ethyl- with 1:3-dimethyl-cyclohexane, *n*- or *iso*-propyl- with 1:1:3-trimethyl-cyclohexane).

The simpler aromatics all have high octane numbers, the latter tending to decrease slightly with increase in the number of carbon atoms (Table II).

Additional information on the relation between antiknock value and the chemical structure of hydrocarbons has been reported by Lovell,

TABLE II.—A.S.T.M. OCTANE NUMBERS  
OF VARIOUS COMPOUNDS.

	A.S.T.M. octane number.
<i>Paraffin hydrocarbons.</i>	
Methane . . . . .	100
Ethane . . . . .	104
Propane . . . . .	100
n-Butane . . . . .	92
2-Methylpropane . . . . .	99
n-Pentane . . . . .	61
2-Methylbutane . . . . .	89
n-Hexane . . . . .	26
2-Methylpentane . . . . .	73
3-Methylpentane . . . . .	75
2:2-Dimethylbutane (Neohexane) . . . . .	96
2:3-Dimethylbutane . . . . .	95
n-Heptane . . . . .	0
2-Methylhexane . . . . .	45
3-Methylhexane . . . . .	66
2:2-Dimethylpentane . . . . .	93
2:3-Dimethylpentane . . . . .	89
2:4-Dimethylpentane . . . . .	82
3:3-Dimethylpentane . . . . .	84
3-Ethylpentane . . . . .	68
2:2:3-Trimethylbutane . . . . .	100
n-Octane . . . . .	-17 (extr.)
2-Methylheptane . . . . .	24
3-Methylheptane . . . . .	35
2:3-Dimethylhexane . . . . .	76
2:5-Dimethylhexane . . . . .	52
3:4-Dimethylhexane . . . . .	85
3-Methyl-3-ethylpentane . . . . .	91
2:2:3-Trimethylpentane . . . . .	102 (extr.)
2:2:4-Trimethylpentane . . . . .	100
2:3:3-Trimethylpentane . . . . .	99
2:3:4-Trimethylpentane . . . . .	96
2:2:3:3-Tetramethylbutane . . . . .	>100
n-Nonane . . . . .	-45 (extr.)
<i>Olefin hydrocarbons.</i>	
Ethylene . . . . .	81
Propylene . . . . .	85
Butene-1 . . . . .	80
Butene-2 . . . . .	83
2-Methylpropene . . . . .	87
Pentene . . . . .	80
2-Methylbutene-2 . . . . .	83-5
Hexene-2 . . . . .	78
Hexene-3 . . . . .	78
2-Methylpentene-2 . . . . .	78
3-Methylpentene-2 . . . . .	77
3:3-Dimethylbutene-1 . . . . .	91
Octene-1 . . . . .	55
<i>cycloParaffin hydrocarbons.</i>	
cyclopentane . . . . .	83
Methylcyclopentane . . . . .	82
cyclohexane . . . . .	77
Methylcyclohexane . . . . .	71
1:3-Dimethylcyclohexane . . . . .	69
Ethylcyclohexane . . . . .	41
n-Propylcyclohexane . . . . .	14
isoPropylcyclohexane . . . . .	61
1:1:3-Trimethylcyclohexane . . . . .	82-5
<i>Aromatic hydrocarbons.</i>	
Benzene . . . . .	106 (extr.)
Toluene . . . . .	104 (extr.)
o-Xylene . . . . .	100
m-Xylene . . . . .	>100
Ethylbenzene . . . . .	98
n-Propylbenzene . . . . .	99
isoPropylbenzene . . . . .	100
1:2:4-Trimethylbenzene . . . . .	91
sec.-Butylbenzene . . . . .	96
tert.-Butylbenzene . . . . .	>100
<i>Alcohols.</i>	
Methyl alcohol . . . . .	91
Ethyl alcohol . . . . .	95
isoPropyl alcohol . . . . .	>100
<i>Ketones.</i>	
Acetone . . . . .	>100
Methyl ethyl ketone . . . . .	>100
Methyl isobutyl ketone . . . . .	>100
<i>Ether.</i>	
Di-isopropyl ether . . . . .	99

Campbell, and Boyd (*ibid.* 1934, 26, 1105). Although they used a different engine and differing engine operating conditions, their conclusions were in many cases similar to those given in this article.

Data on the octane numbers of oxygen compounds are available only in a few cases, but the lower alcohols and ketones have high anti-knock values. While diethyl ether is a pro-knock, diisopropyl ether is nearly equivalent to isooctane. This may be due to the fact that it contains two branched-chain alkyl groups and thus a ketone may be formed on oxidation. Some of the lower ketones have high lead susceptibilities.

A fair degree of correlation has been found between octane number and spontaneous ignition temperature, determined by allowing the fuel to drip into a heated metal pot, the temperature of which is raised until ignition occurs (Weerman, J. Inst. Petroleum Tech. 1927, 13, 300; Egerton and Gates, *ibid.* 1927, 13, 273). Thus branched-chain paraffins have higher spontaneous ignition temperatures than normal paraffins, knock inhibitors increase the spontaneous ignition temperature, etc. The correlation is not perfect, however; diethyl selenide, for example, raises the spontaneous ignition temperature to a greater extent than does tetraethyl lead, though it is a far less effective knock inhibitor (Egerton and Gates, *l.c.*).

When two hydrocarbons are blended in various proportions, the relation between the A.S.T.M. octane number of the blend and the concentration of the component of higher rating is sometimes a straight line, sometimes a curve. In the latter case the octane number of a blend is usually, though not always, less than would be expected from the octane numbers of the pure components. Such curved blending-relationships are usually obtained when one of the components has a Research-Method octane number considerably higher than its Motor-Method octane number, that is, when this component is sensitive to changes in engine conditions. The partial pressure of any fuel component in the fuel-air mixture in the cylinder will, of course, depend on its concentration in the blended fuel; several of the components which exhibit curved blending-relationships are also those the ratings of which are altered considerably by changes in boost pressure (*see* p. 636d).

In considering the problem of relating anti-knock value to chemical structure, it must be remembered that the relative antiknock values of fuels in some cases depend markedly on the operating conditions of the engine. The conclusions given above are based on A.S.T.M. Motor-Method octane numbers and would not necessarily hold under other conditions, for example rich mixture ratings in supercharged engines.

**Knock Inhibitors.**—It has already been mentioned that the oxidation of the fuel in the engine cylinder involves chain reactions. Such reactions are sensitive to inhibitors and several substances have in fact been found to exert an inhibiting action on detonation. These include aniline, other aromatic amines, and certain organometallic compounds, such as diethyl

selenide and telluride, various thallium compounds, nickel and iron carbonyls and tetraethyl lead (Midgley and Boyd, *Trans. Soc. Aut. Eng.* 1920, 15, 659; Boyd, *Ind. Eng. Chem.* 1924, 16, 893; Charch, Mack, and Boord, *ibid.* 1926, 18, 334; C. Ellis, "Chemistry of Petroleum Derivatives," Reinhold, 1937, Vol. II, p. 1016). Pope, Dykstra, and Edgar have obtained chemical evidence that tetraethyl lead inhibits the chain reactions by which hydrocarbons are oxidised (*J. Amer. Chem. Soc.* 1929, 51, 2213). It has been suggested that the effectiveness of this compound is due to its decomposition to lead monoxide and dioxide in the engine, the dioxide decomposing and thus removing organic peroxides formed from the fuel, the lead monoxide formed then reacting with oxygen to reform the dioxide (Egerton and Gates, *J. Inst. Petroleum Tech.* 1927, 13, 281). Withrow and Rassweiler have obtained experimental support for this theory by observing the absorption spectra of the fuel-air mixture before the commencement of combustion in an engine provided with transparent "windows" (*Ind. Eng. Chem.* 1935, 27, 872). Detonation can be effectively reduced by drawing the air supplied to the engine over a lead arc or by the use of a colloidal solution of metallic lead in the fuel.

When tetraethyl lead was first used, trouble was experienced due to pitting of exhaust valves, etc., and the formation of conducting deposits of lead salts on spark plugs. The former difficulty was overcome by the use of special austenitic valve steels and the second by addition of ethylene dibromide to the tetraethyl lead, as a result of which the lead passes out of the exhaust as relatively volatile lead bromide instead of being deposited as lead oxide, etc. The antiknock concentrate supplied for blending with gasoline is called "Ethyl Fluid." The Ethyl Fluid for aviation gasolines contains tetraethyl lead and ethylene dibromide, with small quantities of dye, kerosine, etc., whereas that for motor gasolines contains a proportion of the cheaper ethylene dichloride. The concentration of Ethyl Fluid is always expressed in terms of the active antiknock agent, tetraethyl lead.

The increase in octane number per c.c. of tetraethyl lead per gallon diminishes as the concentration increases. A semi-empirical chart has been devised on which octane number plots as a straight line against tetraethyl lead concentration in a given base gasoline or hydrocarbon, thus permitting "lead" susceptibility to be expressed as a single figure (Hebl, Rendel, and Garton, *ibid.* 1939, 31, 862). In general, paraffins, especially branched-chain paraffins, and cycloparaffins have high lead susceptibilities, while aromatics frequently have low lead susceptibilities. A curious effect of concentration is observed with benzene. As the percentage of benzene in blends with *n*-heptane is increased, the lead susceptibility increases to a maximum at about 63% by volume of benzene, then decreases, becoming negative with pure benzene, i.e., addition of tetraethyl lead to the latter decreases the octane number. Olefins often have relatively low lead susceptibilities. Certain sulphur compounds decrease the lead susceptibility, the effect increasing in the order:

carbon disulphide, thiophen, sulphides, mercaptans, disulphides, and trisulphides, i.e., approximately in the order of reactivity of the sulphur (Birch and Stansfield, *ibid.* 1936, 28, 668). This is possibly due to the partial formation of lead sulphate instead of lead oxides during combustion, lead sulphate being unable to decompose peroxides.

Certain substances, such as ozone, organic nitrites, ether, etc., act as pro-knocks, i.e., they increase detonation. This is thought to be due to their ability to form peroxides.

#### ADDITIONAL SOURCES OF INFORMATION.

For more detailed information and additional references on this subject, the reader is referred to: "Science of Petroleum," 4 Vols., Oxford University Press, 1938.

B. Lewis and G. Von Elbe, "Combustion, Flames and Explosions of Gases," Cambridge University Press, 1938.

Symposium on Gaseous Combustion, *Chem. Rev.*, Oct., Dec., 1937, February, 1938).

F. L. G.

**OCTANE NUMBER (CETANE NUMBER).** The ignition quality of a fuel, i.e., its ability to give smooth running and absence of "knock" in compression-ignition engines, is usually expressed in terms of cetane number. The latter is numerically equal to the percentage by volume of cetane (*n*-hexadecane) which must be mixed with  $\alpha$ -methylnaphthalene to give a blend having the same ignition quality as the test fuel in a compression-ignition engine. Cetane number is less dependent than octane number on the engine and operating conditions, hence standardisation of these factors is of less importance.

**Delay Period.**—In compression-ignition engines (often less accurately called Diesel engines) air is compressed in each cylinder by the motion of the piston and is thus raised to a temperature of the order of 500°C. Shortly before the point of maximum compression, fuel is injected into the combustion chamber as a fine spray, the high temperature of the compressed air causing spontaneous ignition, and the resulting combustion provides the power to drive the engine on the power stroke. Ignition of the fuel is not instantaneous and a short time-lag, the delay period, occurs between injection and ignition. During the injection period fuel is injected continuously and hence unburnt fuel accumulates in the combustion chamber during the delay period. When ignition occurs, this fuel burns with great rapidity causing a rapid increase of pressure, which may give rise to audible knock and rough running of the engine if the delay period is unduly long. Thereafter the rate of burning of the fuel is controlled by the rate at which the fuel is injected. This explanation of the combustion process in compression-ignition engines is due to Ricardo (*Aut. Eng.* 1930, 20, 151).

The sequence of events is illustrated in Fig. 1, in which the pressure in the combustion chamber is plotted against degrees crank-angle. During the delay period the pressure increases at a nearly constant rate. When ignition of the accumulated unburnt fuel occurs there is a rapid increase in pressure, this increase being the more rapid, the longer the delay period.

After this accumulated fuel has been burnt, the pressure increases uniformly at a slower rate, the fuel burning nearly as fast as it is injected, until combustion is completed shortly after the end of the injection period. The pressure then decreases normally during the power stroke.

The delay period is due partly to physical, partly to chemical causes (the physical delay being about 5-10% of the total delay), and depends both on the chemical composition of the fuel and on the engine design and operating conditions. Thus, time is necessary for the fuel droplets to acquire the temperature of the hot compressed air in the cylinder, while the viscosity of the fuel affects the size of the fuel droplets and the extent to which the fuel spray penetrates through the combustion space, thus

finding the air necessary for combustion. The volatility of the fuel is also of some importance from the viewpoint of knock, since ignition starts in the vapour phase and thus a certain amount of vaporisation facilitates ignition, though, if too much vaporisation occurs between injection and ignition, the rate of pressure-rise following ignition may be increased owing to the greater rate of combustion after ignition, thus tending to cause knock (Rothrock, National Advisory Committee for Aeronautics Report No. 435). The fuel must undergo certain preliminary chemical reactions before ignition can occur and the rate which these reactions proceed depends on the chemical composition of the fuel and on the temperature in the combustion space during injection of the fuel.

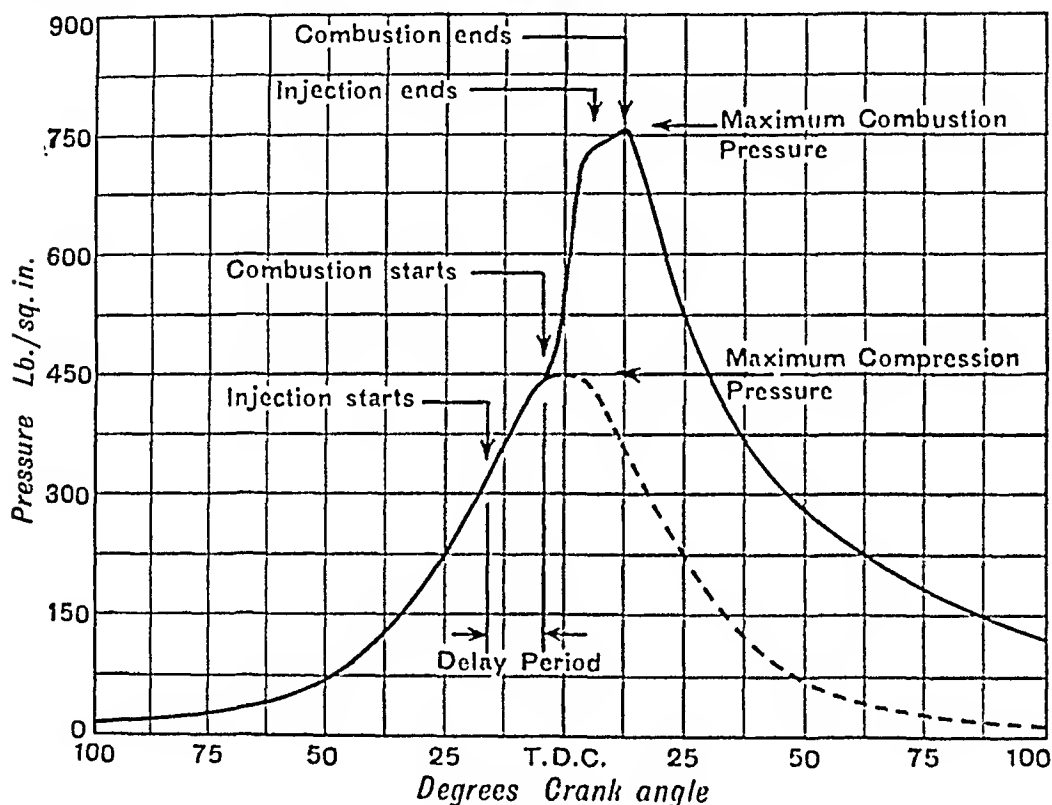


FIG. 1.

Hence those engine factors which affect this temperature will also affect the delay period; these factors include compression ratio, injection advance, speed, temperature and pressure of the intake air, and jacket or cooling air temperature. In addition, degree of mixing of the fuel droplets and air depends on the engine design, while injector design and injection pressure affect the degree of atomisation and penetration of the fuel and also the extent to which the fuel spray fills the combustion space. The total delay period is normally between 0.0004 and 0.005 second.

The physical and chemical properties of the fuel, which affect the delay period, are collectively known as the ignition quality, and the latter is expressed as the cetane number defined as above. The ignition quality of cetane is arbitrarily fixed as 100, that of  $\alpha$ -methyl-naphthalene as 0.

It has been suggested that the chemical reactions which occur during the delay period are oxidation chain-reactions, similar to those which occur with gasoline in spark-ignition engines during the compression stroke. This appears unlikely, however, since the direct oxidation of hydrocarbons by such processes is relatively slow and the time during which the fuel and air are in contact at a high temperature is much shorter in compression-ignition engines. It is more likely that thermal decomposition occurs first, and in fact Boerlage and Van Dijk have found a relation between ignition quality and thermal stability (J. Roy. Aeronaut. Soc. 1934, 38, 953).

Spontaneous ignition temperatures of fuels bear a rough relation to their ignition qualities in an engine, but the correlation is not perfect (Le Mesurier, J. Inst. Petroleum Tech. 1932, 18, 562).

**Measurement of Ignition Quality.**—The pioneer work on the measurement of ignition quality was carried out by Boerlage and Broeze in Holland (Engineering, 1931, 132, 603, 687, 755), by Pope and Murdock in the U.S.A. (Trans. Soc. Aut. Eng. 1932, 27, 136), and by Le Mesurier and Stansfield in England (J. Inst. Petroleum Tech. 1931, 17, 387). Two types of methods have been used. In one type fuels are compared on the basis of delay period (Boerlage and Broeze, *l.c.*), while in the other the engine is motored and the compression pressure varied either by varying the compression ratio (Pope and Murdock, *l.c.*) or by throttling the air intake until the engine will just fire when fuel is injected for a few revolutions.

Previous experience in determining the anti-knock value of gasoline had shown the advantages of using reference fuels, and Boerlage and Broeze proposed the use of *cetene* (hexadecylene) and *mesitylene* as high and low ignition quality standards respectively. Shortly afterwards  $\alpha$ -methyl-naphthalene was substituted for mesitylene on the grounds of price and available supplies. For several years ignition quality was expressed in terms of cetene number. However, owing to variations in different batches of cetene, the (American) Volunteer Group for Compression-Ignition Fuel Research proposed the use of cetane (Trans. Soc. Aut. Eng. 1936, 31, 225), and this has since been widely adopted. On account of the relatively high cost of cetane and  $\alpha$ -methyl-naphthalene, secondary reference fuels are normally employed, the results being converted to cetane numbers by an established conversion curve. The secondary reference fuels normally used are either a high cetane-number paraffinic gas oil and a low cetane-number extract made by treating kerosine with liquid sulphur dioxide (Institute of Petroleum) or a paraffinic gas oil and technical grade methyl-naphthalene (American Society for Testing Materials, abbreviated "A.S.T.M.").

Since the cetane numbers of normal undoped fuels are not markedly affected by the engine and operating conditions used (Boerlage, Broeze, Le Mesurier, and Stansfield, J. Inst. Petroleum Tech. 1936, 22, 455), the two tentative methods standardised by the Institute of Petroleum permit the use of any suitable engine. In method A the delay angle, that is the number of degrees crank-angle between injection and ignition, is determined for the test fuel, and the blend of reference fuels found which gives the same delay angle as the test fuel. In method B an expansion chamber is fitted in the intake pipe and the inlet to this chamber throttled until the engine starts to misfire when using the test fuel; the reference fuel blend which causes misfiring at the same suction pressure as the test fuel is determined. Method A is preferred for routine tests, but method B is convenient, where special apparatus, *e.g.*, for measuring the delay angle, is not available. The two methods give similar results.

The A.S.T.M. method employs a C.F.R. (see this Vol., p. 635a) engine with a specially designed cylinder, the compression ratio of which is continuously variable. The engine is

operated under standardised conditions; tests are carried out with the compression ratio adjusted to give a fixed delay-angle of  $13^\circ$ , and the reference fuel blend, which matches the test fuel, determined. The times of injection and ignition are indicated by instruments of the bouncing-pin type (see OCTANE NUMBER, this Vol., p. 635a).

**Significance of Cetane Number.**—From the section on "Delay Period" it follows that a compression-ignition fuel should normally have a cetane number sufficiently high to give smooth running and freedom from knock in the engines for which it is intended; a higher cetane number than this is of no advantage from this point of view. It must be emphasised that, while an increase in octane number permits the use of higher compression-ratio or greater supercharge, thus increasing efficiency or power output, an increase in cetane number permits the use of lower compression-ratios, which would result in lower efficiency, though permitting a lighter engine.

Low-speed engines (less than about 400 r.p.m.) are not as a rule very critical as regards the cetane number of the fuel, which may be 30 or even less. In high-speed engines (more than about 1,000 r.p.m.) the time available for combustion is reduced and good ignition quality is therefore of greater importance; in these engines fuels with cetane numbers of 45–50 may be required.

Too high a cetane number may be a definite disadvantage in some cases. Thus, if the fuel burned immediately on leaving the injection nozzle, mixing of the air and fuel might be less complete, resulting in incomplete combustion, loss of power, and a smoky exhaust. Further, in certain types of engines the fuel spray is injected diametrically across the combustion space towards a small air-cell connected with the combustion space by a narrow throat; part of the fuel burns in the air-cell and the combustion gases ejected from the cell increase the turbulence and completeness of combustion in the main combustion chamber. If the cetane number of the fuel is too high, and the delay period too short, the fuel may ignite before it reaches the air-cell, thus resulting in incomplete combustion, loss of power, and smoky exhaust as in the previous cases ("The Evaluation of Petroleum," 1940, p. 32, publ. by American Society for Testing Materials).

Starting an engine from cold tends to be more difficult at low atmospheric temperatures because the low air temperature of itself reduces the maximum compression temperature and no heat is radiated from the cylinder and piston until the engine warms up. The delay period is therefore longer and in some cases starting may be impossible. Under these circumstances higher cetane-number fuels improve ease of starting. Such fuels are also advantageous for operating at high altitudes, where the low intake-air pressure reduces the compression temperature and hence increases the delay.

There is much more chance for regions of over-rich fuel-air mixtures to exist in the combustion space with compression-ignition than with spark-ignition engines. This results in thermal decom-

position of the fuel to "carbon," etc., causing a smoky exhaust, deposition of carbon on injector nozzles, etc., especially at full throttle and with fuel of too low a cetane number. Under comparable conditions exhaust smoke tends to increase as the cetane number of the fuel is reduced.

In certain engines a kind of lacquer may be deposited on the pistons, causing sticking of the piston rings and even seizure of the piston in the cylinder within a short time, with fuels of too low cetane number; this occurs especially during part throttle operation, when engine temperatures are relatively low. This lacquer is composed of organic acids, polymerised aldehydes, etc., and is apparently formed by chilling of the combustion by the relatively cool cylinder walls (Boerlago and Broeze, *Ind. Eng. Chem.* 1936, 28, 1229). According to these authors the combustion process is probably a combination of thermal decomposition and hydroxylation (W. A. Bone and D. T. A. Townend, "Flame and Combustion in Gases," Longmans, 1927, p. 373), intermediate products from the latter process giving rise to lacquer. The acrid odour sometimes noticeable in the exhaust from compression-ignition engines at light loads has been shown to be due to aldehydes, probably formed in a similar way. Lacquer and exhaust-odour tend to be greater with lower cetane-number fuels.

Further information on the relation between cetane number and the various performance characteristics mentioned above are given by Ainsley, Young, and Hamilton (*Trans. Soc. Aut. Eng.* 1942, 50, 160) and Wetmiller and Endsley (*ibid.*, p. 509).

In compression-ignition engines knock tends to increase, the slower burning the fuel, while the reverse is true in spark-ignition engines. As a result there is an inverse relationship between cetane number and octane number.

**Relation between Chemical Structure and Cetane Number.**—The ignition qualities of pure hydrocarbons have been determined in a few cases only. However, some information is obtainable from hydrocarbon type-analyses of various compression-ignition fuels. Thus the indications are that ignition quality decreases in the order (i) normal paraffins, (ii) olefins, (iii) aromatics; branched-chain paraffins have lower ignition qualities, the greater the degree of branching (Boerlago and Broeze, *ibid.* 1932, 27, 283), the octane numbers of *n*-heptane and 2:2:4-trimethylpentane, for example, being 64 and 22 respectively. Ju, Wood, and Garner from a study of blends each containing 50% of *n*-alkylbenzene find a steady increase in blending cetane number from toluene (−21) to *n*-tetradecylbenzene (72), though the first member, benzene, has a cetane number of −10 (*J. Inst. Petroleum*, 1942, 28, 159). No information on cycloparaffins appears to be available.

Several "indices," which bear a rough relation to chemical structure, have been proposed to replace engine tests as a measure of ignition quality. Of these the most widely used is the Diesel Index (Becker and Fischer, *Trans. Soc. Aut. Eng.* 1934, 29, 376).

$$\text{Diesel Index} = \frac{\text{Anilino point (°F.)} \times \text{A.P.I. gravity}}{100}$$

Anilino point is the minimum temperature at which equal volumes of anilino and the fuel are completely miscible, while A.P.I. (American Petroleum Institute) gravity is defined as:

$$\text{A.P.I. gravity} = \frac{141.5}{\text{Specific gravity}} - 131.5$$

Diesel Index shows a fairly good correlation with cetane number in many cases and has been successfully used for routine control of fuels of known origin. There are exceptions, however, and it is not a satisfactory guide for fuels of unknown origin; furthermore it fails completely with fuels consisting largely of branched-chain paraffins and with fuels containing small quantities of ignition accelerators (*see below*). Other indices based on viscosity and specific gravity (Moore and Kaye, *Oil and Gas J.* 1934, Nov. 15, p. 108), boiling-point and gravity (Jackson, *Oil and Gas J.* 1935, Mar. 21, p. 16) or on the paraffin (Heinze and Marder, *Brennstoff-Chem.* 1935, 16, 286) have been proposed, but have not been so widely used as Diesel Index. Recently the Institute of Petroleum have recommended the following formula for normal undoped fuels (*J. Inst. Petroleum*, 1944, 30, 193):

$$\text{Calculated cetane no.} = 175.4 \log (\text{mid-boiling point, °F.}) + 1.98(\text{A.P.I. gravity}) - 496$$

**Ignition Accelerators.**—Several materials have been discovered, small quantities of which considerably increase the cetane number of compression-ignition fuels, though none approaches the effectiveness of tetraethyl lead in raising the octane number of gasoline. However, the more effective will increase the cetane number of a fuel by 6–13 units at a concentration of 0.5% by weight. These substances include organic peroxides, nitrates, nitrites, thio-nitrites, di-, and poly-sulphides, triazenes, chloropierin, etc. Data on a large number of these ignition accelerators have been summarised by Bogen and Wilson, *Petroleum Refiner*, 1944, 23, No. 7, 118, where additional references will be found. The increase in cetane number is usually greater, the higher the cetane number of the base stock, and the effectiveness decreases with concentration.

Broeze and Hinzo explain the action of ignition accelerators by a chain-reaction mechanism (*J. Inst. Petroleum*, 1939, 25, 657), but little experimental evidence on this subject appears to have been published.

F. J. G.

**OCTOIC ACIDS.** The most important of the 39 possible isomeric fatty acids of the formula  $C_7H_{15}\cdot COOH$  is *n*-octoic acid (caprylic, heptane-1-carboxylic acid). This is of wide natural occurrence as esters, glycerides, and as the free acid in many oils and fats of animal, vegetable, and mineral origin. It is among the fatty acids obtained by the saponification of various fats, e.g., coconut oil (8.7%) (Taylor and Clarke, *J. Amer. Chem. Soc.* 1927, 49, 2829), palm kernel oil (3%) (Armstrong, Allan, and Moore, *J.S.C.I.* 1925, 44, 143r), cohune nut



fat (7.5%) (Hilditch and Vidyarthi, *ibid.* 1928, 47, 35r), butter fat (1.3–2%) (see BUTTER, Vol. II, 161), Japanese sardine oil (J. Soc. Chem. Ind. Japan, 1940, 43, 59) and in goat butter-fat (together with caproic and capric acids), and from which the name caprylic acid is derived (L. caper-pri, goat). *n*-Octoic acid is present as esters in small quantities in the odorous constituents of apples and peaches (Power and Chesnut, J. Amer. Chem. Soc. 1920, 42, 1513; 1921, 43, 1725) and in the volatile constituents of Valencia orange juice (Hall and Wilson, *ibid.* 1925, 47, 2575). Other sources include orange peel oil, orris oil, oil of rue, fusel oil, tobacco flowers, and Limburger cheese. (The flavour of roquefort cheese is due to fatty acids, including *n*-octoic acid, liberated from the butter fats by the lipases of the mould.) It has also been isolated from petroleum acids (Quebedeaux, Wash, Ney, Crouch, and Lochte, *ibid.* 1943, 65, 767).

It may be prepared by fractionating the fatty acids obtained by the saponification of coconut oil, the portion boiling 220–240° being converted into the barium salt and purified by recrystallisation. The free acid is then liberated and distilled (Van Renesse, *Annalen*, 1874, 171, 380). Although synthetic methods may be employed, as the condensation of two molecules of aldol with subsequent oxidation and reduction of the product (Raper, J.C.S. 1907, 91, 1831), or by oxidation of *n*-octyl alcohol, the isolation from natural sources is more economical, and the acid so prepared is used for the preparation of other *n*-octyl derivatives (e.g., *n*-octyl alcohol, by the reduction of ethyl caprylate with sodium and alcohol (J. Amer. Chem. Soc. 1922, 44, 2648)).

*n*-Octoic Acid, m.p. 16.3°, b.p. 239.7°/760 (for boiling-point at lower pressures, see Pool and Ralston, Ind. Eng. Chem. 1942, 34, 1104),  $\rho_4^{20}$  0.914,  $\lambda_D^{25}$  1.41  $\times 10^{-5}$ , solubility in water at 15°: 0.072 g./100 c.c. *Methyl ester*, b.p. 193–194°; *ethyl ester*, b.p. 207–208°; *propyl ester*, b.p. 225°; and *n-butyl ester*, b.p. 240.5°; *glyceryl tri-n-octoate*, m.p. 8°. *Copper salt*, m.p. 264–266°; *zinc salt*, m.p. 135–136°; *lead salt*, m.p. 83–84°. *Anhydride*, b.p. 280–285°; *acid chloride*, b.p. 194–196°; *amide*, m.p. 110°; *nitrile*, b.p. 198–200°.

Passage of the vapours of *n*-octoic acid over ferrous or ferric oxide at 450–490° gives a 77% yield of *di-n-heptyl ketone*, m.p. 39° (Mailhe, Compt. rend. 1913, 157, 220); if mixed with formic acid and passed over titanium dioxide at 300° it gives a 90% yield of octanal (caprylaldehyde). Certain micro-organisms, such as *penicillium glaucum*, convert the acid into methyl amyl ketone (by  $\beta$ -oxidation to  $\beta$ -keto-octoic acid, followed by decarboxylation), and it is ketones of this type, having unpleasant odours, which are the cause of the rancid odours of fats (e.g., cocoa-butter) attacked by moulds.

A compound with triethanolamine has been recommended as a wetting agent for use in the textile industry or in ore treatment (U.S.P. 2239997), and the use of heavy metal salts has been suggested as mordants in steam printing (Pomeranz, Amer. Chem. Abstr. 1932, 26, 3931). A solution in water (1:5,000) has been suggested as an insecticide (J. Agric. Res. 1924, 29, 259). The preparation of therapeutic esters of œstrone, equilin, and equilenin with *n*-octoic acid has been patented (U.S.P. 2228397), and also œstradiol di-*n*-octoate (Swiss P. 205439).

B. A. K.  
OCTYL is the monovalent radical  $C_8H_{17}$ , which would result theoretically from the removal of one hydrogen atom from an octane  $C_8H_{18}$ . From the 18 known isomeric octanes it is possible to derive 89 isomeric octyl radicals (excluding stereoisomers). Unless otherwise stated, octyl may be taken to refer to normal octyl  $CH_3[CH_2]_6CH_2$ . The existence of octyl as a free radical of short life has not been demonstrated.

OCTANES.

Octanes occur in many crude oils and associated natural gases, but the amounts vary widely. The natural gasoline recovered from gas associated with the light paraffinic Pennsylvania oil has been shown to contain about 4% octane (Anderson and Erskine, Ind. Eng. Chem. 1924, 16, 263). The 55–145° fraction of Ponca, Oklahoma oil (a fairly typical mid-continent crude) contains about 11.1% of octanes, *n*-octane accounting for 7% and eight other isomers for 4.1%.

TABLE I.—ISOMERIC OCTANES.

	Isomer.	M.p.	B.p. at 760 mm.	$\rho_4^{20}$	$n_D^{20}$	Octane number.
1.	<i>n</i> -Octane . . . . .	–56.8°	125.6°	0.70283	1.39764	–17
2.	2-Methylheptane . . . .	–111.3°	117.2°	0.6978	1.3947	24
3.	3-Methylheptane . . . .		119°	0.7057	1.3983	35
4.	4-Methylheptane . . . .		118°	0.7163	1.39814	
5.	3-Ethylhexane . . . . .		113.9°	0.7122	1.4020	
6.	2,2-Dimethylhexane . . .		107°	0.6956	1.3930	
7.	2,3-Dimethylhexane . . .		115.7°	0.71240	1.40117	76
8.	2,4-Dimethylhexane . . .		109°	0.6993	1.39582	
9.	2,5-Dimethylhexane . . .	–90.7°	109.3°	0.6949	1.39295	52
10.	3,3-Dimethylhexane . . .		111°	0.7086	1.3993	
11.	3,4-Dimethylhexane . . .		117.8°	0.7195	1.4045	85
12.	2-Methyl-3-ethylpentane .		114°	0.7182	1.4033	
13.	3-Methyl-3-ethylpentane .		118.4°	0.7256	1.4031	91
14.	2,2,3-Trimethylpentane . .		110.3°	0.7162	1.4032	102
15.	2,2,4-Trimethylpentane . .	–107.45°	99.3°	0.69194	1.39157	100
16.	2,3,3-Trimethylpentane . .		114.2°	0.7258	1.4075	99
17.	2,3,4-Trimethylpentane . .		113.4°	0.7195	1.4046	97
18.	2,2,3,3-Tetramethylbutane .	–101°	106.5°			103

Owing to the importance of octanes in petrol, and especially highly branched isomers in high-octane aviation spirit, much research has been done on the production of octanes by cracking of crude oil, by polymerisation, and by alkylation methods and which are now carried out on a large scale industrially. In addition, many isomers have been synthesised on a fairly large laboratory scale using unequivocal methods, and after careful purification by fractional distillation, the physical constants have been recorded for use in the identification of constituents of petroleum and cracked petroleum products.

All the 18 possible isomeric octanes are known and are listed in Table I together with some physical properties. (For greater detail, see G. Egloff, "Physical Constants of Hydrocarbons," Reinhold, New York, 1939, Vol. I.)

Octane Number (see this Vol., p. 632e).

#### Laboratory Preparation of Octanes.

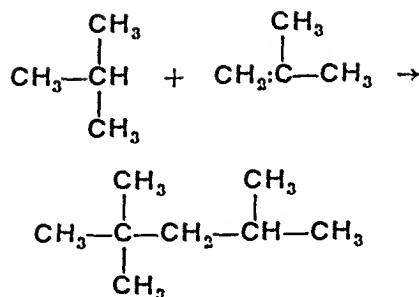
The dehydration of an octanol to an octene followed by catalytic hydrogenation is a method of wide application. Symmetrical isomers may be made by the Wurtz synthesis or by electrolysis of potassium salts. The interaction of zinc dialkyls and alkyl halides, the reduction of halides, etc., have also been employed. Hexamethylethane offers certain experimental difficulties, but has been prepared in 16% yield from *tert.*-butyl magnesium chloride and *tert.*-butyl iodide (Marker and Oakwood, J. Amer. Chem. Soc. 1938, 60, 2598).

#### Industrial Preparation of Octanes.

Very large quantities of  $C_4$  hydrocarbons (*n*-butane, butene-1, butene-2, isobutane and isobutene) are produced in the cracking of petroleum and can be converted to petrol hydrocarbons by various processes.

If the mixture is passed through 65% sulphuric acid, the isobutene is removed more than 100 times as fast as butene-1 or butene-2, and heating to 100° causes dimerisation to "di-isobutene," a mixture of 2:4:4-trimethylpentene-1 and 2:4:4-trimethylpentene-2, which separates as an oily layer, and the acid can be used again. The "di-isobutene" is then hydrogenated to 2:2:4-trimethylpentane ("iso-octane") (Sparks, Rosen, and Frölich, Trans. Faraday Soc. 1939, 35, 1040; Whitmore, Ind. Eng. Chem. 1934, 26, 94). Various other catalysts may be employed, e.g., copper cadmium phosphato (Birch and Dunstan, Trans. Faraday Soc. 1939, 35, 1013), copper pyrophosphate (Van Voorhis, Nat. Petroleum News, 1940, 32, 230R), or the dimerisation and hydrogenation may be carried out simultaneously in the presence of phosphoric acid-nickel oxide-iron catalyst (Ipatiev, Komarevsky, Ind. Eng. Chem. 1937, 29, 958).

Another process is the "alkylation" of an alkane with an alkene, an important application being the production of 2:2:4-trimethylpentane in high yield from isobutane and isobutene in the presence of 97% sulphuric acid at 20° (Birch and Dunstan, *loc. cit.*; Birch, Dunstan, Pim, Fidler, and Tait, *ibid.* 1939, 31, 1079; B.P. 479345).



The alkylation of isobutane with a mixture of butene-1 and butene-2 at -35° using aluminium chloride gives *iso*-octanes and *isododecanes* in a 5:1 ratio, the *iso*-octane fraction being composed of 2:2:3- and 2:2:4-trimethylpentanes, showing that some *n*-butenes have probably been isomerised to isobutene (Pines, Gosse, and Ipatiev, J. Amer. Chem. Soc. 1942, 64, 33).

By a combination of processes of the types above almost the whole of the  $C_4$  hydrocarbon fraction can be converted into high octane petrol, except *n*-butane, which is easily separated and either isomerised to isobutane or dehydrogenated to butenes and added to the next charge.

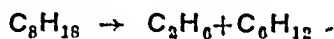
Since the octane number is a function of molecular structure, and *n*-octane, the predominating naturally occurring isomer, has the lowest octane number of any octane, it is clear that isomerisation would lead to a higher grade fuel. Sivertzev (J. Gen. Chem. Russ. 1940, 10, 799) has shown that a 22-hour treatment of *n*-octane at room temperature with 10% aluminium chloride and 10%  $\text{PbSO}_4 \cdot 2\text{HCl}$  gave 24.3% of branched octanes. Petrov, Meschtscherjakov, and Andreev (Ber. 1935, 68 [B], 1) found that *n*-octane is partially isomerised when heated with a catalyst during 3 hours at 410°/70 atm. initial pressure, the yield of isomers depending on the catalyst employed as follows: aluminium chloride gave 23.3%, molybdenum trisulphide 18%, and zinc chloride 11.7%. Nickel alumina, nickel on zinc oxide, and platinum on activated charcoal will catalyse the isomerisation of *n*-octane at atmospheric pressure and 300-310°; yield 6.4-15% isomers (Juriev and Pavlov, J. Gen. Chem. Russ. 1937, 7, 97).

#### Chemical Properties of Octanes.

1. *Cracking*.—*n*-Octane is decomposed (80-90%) on heating to 500-570°, the reaction going in two directions:



and

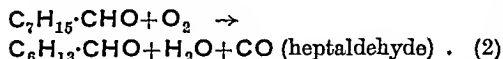
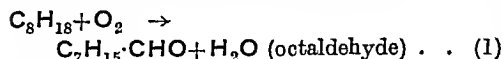


and the olefins formed are then largely decomposed (60-70%) into  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $C_3H_6$ , and  $C_4H_8$  (Dintzes and Frost, *ibid.* 1934, 4, 610). Treatment of *n*-octane in the glow discharge at 0.5-10 mm. yields 48.9%  $H_2$ , 13.8% acetylenes, 16.6% olefins, and 20.8% paraffins (Linder and Davis, J. Physical Chem. 1931, 35, 3649). The thermal decomposition in the presence of various catalysts has been studied, e.g., magnesium, to give 58%  $Mg_2C_3$  at 700° (Novak, Z. physikal. Chem. 1911, 73, 513), aluminium chloride, etc.

2. *Dehydrocyclisation*.—Heating in the presence of metallic oxides (especially of group IV, V, and VI metals) converts octanes into alkyl benzenes in high yield; titanium, zinc, or molybdenum oxides at 400–505° converts *n*-octane into *o*-xylene (Moldavski, Kamuscher, and Kolilskaja, *J. Gen. Chem. Russ.* 1937, 7, 1835); 2,5-dimethylhexane gives 80% *p*-xylene with chromic oxide (Kazanski, Liberman, Plate, Serguienko, and Zelinsky, *Compt. rend. Acad. Sci. U.R.S.S.* 1940, 27, 446); 3-methylheptane gives *o*-, *m*-, and *p*-xylenes and only a little ethylbenzene.

3. *Nitration*.—Vapour-phase nitration of *n*-octane by means of  $N_2O_4$  at 200° gives a mixture of mono- (81%) and di-nitro-octanes (19%) (Urbański and Słoń, *Compt. rend.* 1937, 204, 870).

4. *Oxidation*.—A detailed study of the oxidation of *n*-octane has been made by Pope, Dykstra, and Edgar (*J. Amer. Chem. Soc.* 1929, 51, 1875), and the hypothesis advanced that oxidation occurs by stepwise degradation:



followed by repetition of reactions of the type (2) to give lower aldehydes. The oxidation of the aldehydes proceeds by luminescent chain-reactions, which may be correlated with the tendency to "knock." If branched-chain hydrocarbons are oxidised, the degradation of the carbon chain is retarded when a branch is reached, and this may account for the low "knocking" characteristics of highly branched octanes. The chain reactions are also retarded by lead tetraethyl, used as an "antiknock" agent.

5. *Isomerisation*.—*v. supra*.

#### OCTENES (OCTYLENES).

Of the 66 possible isomeric octenes (excluding geometrical and stereoisomers), 62 are listed with physical properties by Egloff (*op. cit.*).

Geometrical isomerism is possible in many octenes but usually synthesis leads to a *cis-trans* mixture and only in a very few cases have the two isomers been isolated. Young, Jasaitis, and Levanas (*ibid.* 1937, 59, 403) obtained *cis*- and *trans*-octene-4 by the action of a zinc-copper couple on *dl*- and *meso*-4,5-dibromo-octane, and Van Risseghem (*Bull. Soc. chim. Belg.* 1938, 47, 194) prepared *cis*- and *trans*-octene-3 by a similar method.

Two of the most important octenes are 2:2:4-trimethylpentene-1 (m.p. -93.7°, b.p. 101.5°,  $\rho_4^{20}$  0.7164,  $n_D^{20}$  1.4089) and 2:2:4-trimethylpentene-2 (m.p. -107°, b.p. 104.5°,  $\rho_4^{20}$  0.722,  $n_D^{20}$  1.4159) obtained as a mixture ("di-isobutene") by dimerisation of isobutene (*v. supra*). Oxidation of the mixture gives methyl neopentyl ketone  $CH_3 \cdot CO \cdot CH_2 \cdot CMe_3$  in reasonable yield.

The four normal octenes have boiling-points as follows: octene-1, 122.5°; octene-2, 125°; octene-3, 122–123°; and octene-4, 122°.

In the presence of an activated silica-alumina catalyst at 375–400°, a mixture of octene-1 and octene-2 undergoes catalytic isomerisation to isooctenes, followed by catalytic cracking to gaseous products consisting principally of equal amounts of *n*- and *iso*-butane. For the preparation of branched octenes from normal octenes, the use of a silica-alumina-thoria catalyst (U.S.P. 2216284) and sodium permutterite (U.S.P. 2217252) has been recommended.

#### OCTYL ALCOHOLS.

Over 50 of the 89 possible isomeric octyl alcohols have been described and are listed in Table II, together with the boiling-point, one method of preparation, and the corresponding reference.

The method of widest application for their synthesis is the reaction of an alkyl magnesium halide with an aldehyde, ketone, ester or olefin oxide. Primary octanols can often be conveniently prepared by the reduction of an ethyl ester in toluene using sodium and alcohol, and secondary ones by reduction of the corresponding ketone with sodium and moist ether.

A comprehensive study of the four straight chain octanols (Nos. 1–4) and the eighteen isomeric methyl heptanols (Nos. 5–22) has been made by Dorough, Glass, Gresham, Malone, and Reid (*J. Amer. Chem. Soc.* 1941, 63, 3100) and for carefully purified samples the data recorded include the b.p. at 20, 100, 300, and 760 mm., latent heat of evaporation,  $\rho_4^{25}$ ,  $\rho_4^{25}$ , coefficients of expansion,  $n_D^{25}$ ,  $M_D$ , m.p., solubility in water, surface tension and energy, dielectric constant, rate of esterification with acetic acid, toxicity, etc.

For these 22 isomers the values ranged as follows: b.p. 153.4°–195°, m.p. -123 to -15°,  $\rho_4^{25}$  0.7766–0.8335,  $n_D^{25}$  1.4113–1.4275 and the solubility in water at 25° from 0.538 to 3.373 g. per kilo.

Many of the isomers when synthesised are obtained as *dl*-mixtures and resolution into the optically active forms has been achieved with alcohols marked \* in Table II. The fractional crystallisation of the brucine or strychnine salts of the half esters with phthalic acid is the usual method employed (see "Organic Reactions," Wiley, New York, 1944, Vol. II, 376).

Space will permit the brief individual mention of the two commoner isomers only, i.e., *n*-octyl and *sec*-octyl alcohol.

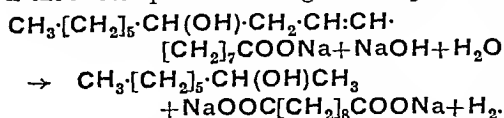
*n*-Octyl Alcohol,  $CH_3[CH_2]_6CH_2OH$ , occurs as the acetate and butyrate in certain plants, especially of genus *Heracleum*. It is a colourless liquid with an aromatic odour, b.p. 100.7°/20 mm., 164°/300 mm., and 195°/760 mm.,  $\rho_4^{20}$  0.8394,  $\rho_4^{25}$  0.8224,  $n_D^{25}$  1.4275, m.p. -15°, surface tension 24.58 dynes per sq. cm. at 20°, and solubility in water 0.538 g. per kilo at 25°. 3:5-Dinitrobenzoate, m.p. 62°,  $\alpha$ -naphthylurethane, m.p. 66°, phenyl urethane, m.p. 74°, and *p*-xyleneurethane m.p. 110°. The *p*-nitrobenzyl ester is an oil.

*sec*-Octyl Alcohol,



Isomer.	B.p.	One method of preparation.	Reference.
1. 1-Octanol . . . . .	195°	Reduction of $\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{Et}$	J. Amer. Chem. Soc. 1922, 44, 2048.
2. 2-Octanol . . . . .	180°	Na ricinolate + NaOH	Organic Syntheses, 1941, Coll. Vol. I, 300.
3. 3-Octanol . . . . .	173°	Reduction of $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{C}_2\text{H}_5$	J.C.S. 1913, 103, 1944.
4. 4-Octanol . . . . .	176-3°	Reduction of $\text{C}_3\text{H}_7\text{CO}_2\text{CH}(\text{OH})\text{C}_2\text{H}_5$	Compt. rend. 1905, 140, 1700.
5. 5-Octanol . . . . .	175-4°	$\text{CH}_3(\text{CH}_2)_4\text{CHMeMgBr} + \text{HCHO}$	J. Amer. Chem. Soc. 1941, 63, 3100.
6. 6-Octanol . . . . .	166-1°	$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{Et} + \text{MeMgI}$	Compt. rend. 1901, 132, 483.
7. 7-Octanol . . . . .	167-2°	Reduction of $\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{CHMe}_2$	J.O.S. 1912, 101, 629.
8. 8-Octanol . . . . .	160-3°	$\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{CHMe}_2\text{CHO}$	Compt. rend. 1906, 143, 102.
9. 9-Octanol . . . . .	187-0°	Reduction of $\text{CHMe}_2(\text{CH}_2)_2\text{CO}_2\text{Et}$	J. Biol. Chem. 1916, 27, 453.
10. 10-Octanol . . . . .	171-8°	Reduction of $\text{CHMe}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	Annalen, 1915, 408, 185.
11. 11-Octanol . . . . .	153-5°	$\text{CHMe}_2\text{CH}_2\text{CH}_2\text{MgI} + \text{C}_2\text{H}_5\text{CHO}$	Compt. rend. 1906, 143, 102.
12. 12-Octanol . . . . .	195-8°	Reduction of $\text{C}_4\text{H}_9\text{CHMe}_2\text{CO}_2\text{Et}$	J. Biol. Chem. 1931, 91, 77.
13. 13-Octanol . . . . .	190-4°	$\text{CH}_3(\text{CH}_2)_3\text{CHMe}_2\text{MgBr} + \text{CH}_3\text{CHO}$	J. Amer. Chem. Soc. 1941, 63, 3100.
14. 14-Octanol . . . . .	159-4°	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{MgBr} + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	Rec. trav. chim. 1927, 46, 408.
15. 15-Octanol . . . . .	161-7°	$\text{CH}_3\text{MeCHMe}_2\text{MgBr} + \text{CH}_3\text{CH}_2\text{CHO}$	J. Amer. Chem. Soc. 1941, 63, 3100.
16. 16-Octanol . . . . .	196-5°	$\text{C}_2\text{H}_5\text{CHMe}_2\text{CH}_2\text{MgBr} + (\text{CH}_2)_2\text{O}$	<i>Ibid.</i>
17. 17-Octanol . . . . .	171-0°	$\text{C}_2\text{H}_5\text{CHMe}_2\text{CH}_2\text{MgBr} + \text{CH}_3\text{CHO}$	<i>Ibid.</i>
18. 18-Octanol . . . . .	153-4°	$\text{C}_2\text{H}_5\text{CHMe}_2\text{CH}_2\text{MgBr} + (\text{CH}_3)_2\text{O}$	<i>Ibid.</i>
19. 19-Octanol . . . . .	182-7°	Reduction of $\text{C}_2\text{H}_5\text{CHMe}_2\text{CO}_2\text{Et}$	J. pr. Chem. 1914, 80, 453.
20. 20-Octanol . . . . .	171-7°	Reduction of $\text{C}_2\text{H}_5\text{CHMe}_2\text{CO}_2\text{CH}_3$	J. Biol. Chem. 1932, 54, 351.
21. 21-Octanol . . . . .	155-4°	$\text{CH}_3\text{BrCOBr} + \text{ZnEt}_2$	J. Amer. Chem. Soc. 1912, 34, 670.
22. 22-Octanol . . . . .	160-8°	Reduction of $\text{CH}_3\text{CHMe}_2\text{CONH}_2$	<i>Ibid.</i> , p. 677.
23. 23-Octanol . . . . .	181°	$\text{C}_2\text{H}_5\text{CHMe}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{MgBr}$	Annalen, 1878, 191, 140.
24. 24-Octanol . . . . .	103°	$\text{C}_2\text{H}_5\text{CO}_2\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{MgI}$	Bull. Soc. chim. 1923, [iv], 43, 345.
25. 25-Octanol . . . . .	153-159°	$\text{CH}_3\text{BrCOBr} + \text{ZnEt}_2$	J. Amer. Chem. Soc. 1926, 51, 1253.
26. 26-Octanol . . . . .	181-106°	(Obtained as <i>tert</i> -butylacetate ester.)	<i>Ibid.</i> , 1933, 60, 2402.
27. 27-Octanol . . . . .	93-729 mm.	$\text{CH}_3\text{CO}_2\text{CHMe}_2 + \text{C}_2\text{H}_5\text{MgBr}$	<i>Ibid.</i> , 1911, 33, 529.
28. 28-Octanol . . . . .	153-156°	$\text{CH}_3\text{CHMe}_2\text{CO}_2\text{CH}_2 + \text{CH}_3\text{MgI}$	<i>Ibid.</i> , p. 523.
29. 29-Octanol . . . . .	150-151°	$\text{CH}_3\text{CO}_2\text{CHMe}_2 + \text{C}_2\text{H}_5\text{MgBr}$	Ind. Eng. Chem. 1931, 23, 1381.
30. 30-Octanol . . . . .	61-62/13 mm.	From catalytic reduction of CO with $\text{H}_2$ (?)	J. Amer. Chem. Soc. 1903, 30, 1150.
31. 31-Octanol . . . . .	173-175°	$\text{C}_2\text{H}_5\text{CHMe}_2\text{CH}_2\text{CO}_2\text{CH}_3 + \text{CH}_3\text{MgI}$	<i>Ibid.</i> , p. 1147.
32. 32-Octanol . . . . .	150°	$\text{C}_2\text{H}_5\text{CHMe}_2\text{CH}_2\text{CO}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{MgI}$	J. Biol. Chem. 1932, 95, 1.
33. 33-Octanol . . . . .	131°	Reduction of $\text{CHMe}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$	J.C.S. 1879, 35, 126.
34. 34-Octanol . . . . .	105-145 mm.	Hydrolysis of $\text{CHMe}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$	Compt. rend. 1911, 152, 108.
35. 35-Octanol . . . . .	179-180°	Reduction of $\text{CH}_3\text{CHMe}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{MgBr}$	Chem. Zentr. 1912, 1, 1100.
36. 36-Octanol . . . . .	157-158°	$\text{CHMe}_2\text{CH}_2\text{CH}_2\text{MgBr} + \text{CHMe}_2\text{CHO}$	J. Amer. Chem. Soc. 1933, 55, 1550.
37. 37-Octanol . . . . .	76-6°/15 mm.	$\text{CHMe}_2\text{CO}_2\text{CH}_2 + \text{CH}_3\text{MgBr}$	Amer. Chem. J. 1903, 39, 574.
38. 38-Octanol . . . . .	156°	$\text{CHMe}_2\text{CO}_2\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{MgBr}$	Bull. Soc. chim. Belg. 1926, 35, 384.
39. 39-Octanol . . . . .	172°	Reduction of $\text{CH}_3\text{CO}_2\text{CHMe}_2$	Amer. Chem. J. 1903, 39, 578.
40. 40-Octanol . . . . .	75-73°/12 mm.	$\text{C}_2\text{H}_5\text{MgCl} + \text{HCHO}$	J. Amer. Chem. Soc. 1933, 58, 1560.
41. 41-Octanol . . . . .	149-152°	$\text{CHMe}_2\text{CO}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{MgBr}$	<i>Ibid.</i> , 1912, 34, 173.
42. 42-Octanol . . . . .	101-107°	$\text{CHMe}_2\text{CO}_2\text{CH}_2 + (\text{CHMe}_2)_2\text{O}$	Bull. Soc. chim. 1925, [iv], 37, 1555.
43. 43-Octanol . . . . .	150-151°	$\text{CMe}_2\text{MgCl} + \text{CHMe}_2\text{CHO}$	J. Amer. Chem. Soc. 1920, 51, 1233.
44. 44-Octanol . . . . .	70°/13 mm.	$\text{CMe}_2\text{CH}_2\text{CO}_2\text{CH}_2 + \text{CH}_3\text{MgBr}$	<i>Ibid.</i> , 1912, 64, 2070.
45. 45-Octanol . . . . .	82-83°/50 mm.	$\text{Me}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CHMe}_2\text{MgBr} + \text{CH}_3\text{COCl} + \text{CH}_3\text{MgBr} \end{array}$	<i>Ibid.</i> , 1930, 58, 2147.
46. 46-Octanol . . . . .	155-157°	$\text{CHMe}_2\text{CO}_2\text{CHMe}_2 + \text{CH}_3\text{MgBr}$	<i>Ibid.</i> , 1930, 61, 69.
47. 47-Octanol . . . . .	156-5°	$\text{CHMe}_2\text{CO}_2\text{CHMe}_2 + \text{CH}_3\text{MgBr}$	Bull. Soc. chim. Belg. 1920, 35, 381.
48. 48-Octanol . . . . .	149-150°	$\text{CMe}_2\text{CO}_2\text{CH}_2 + \text{O}_2$	J. Amer. Chem. Soc. 1911, 63, 1626.

(Capryl alcohol), is readily prepared by heating castor oil with sodium hydroxide (Organic Syntheses, 1941, Coll. Vol. I, 366). Saponification of the oil gives sodium ricinoleate, which is then decomposed according to the equation:



The *dl*-product obtained can be resolved if desired (*ibid.*, p. 418).

The *dl*-alcohol has b.p. 87.6°/20 mm., 120.5/100 mm., 149.3°/300 mm., and 180.0°/760 mm.,  $\rho_4^{25}$  0.8170,  $\rho_4^{20}$  0.8353,  $n_D^{25}$  1.4238, m.p. -31.6°, surface tension 22.97 dynes per sq. cm. at 20°, solubility in water 0.955 g. per kilo. at 25°. 3:5-Dinitrobenzoate, m.p. 32°,  $\alpha$ -naphthylurethane, m.p. 63°, p-nitrobenzoate 28°. The phenylurethane is an oil.

#### OTHER OCTYL COMPOUNDS.

**Halides:** *n*-Octyl fluoride, b.p. 142.5°; chloride, b.p. 184°; bromide, b.p. 201.5°; iodide, b.p. 225.5°. *sec*-Octyl fluoride, b.p. 139.30°; chloride, b.p. 75°/28 mm.; bromide, b.p. 72°/14 mm.; iodide, b.p. 190°.

**Esters:** *n*-Octyl formate, b.p. 198.1°; acetate, b.p. 210°; propionate, b.p. 266.4°; butyrate, b.p. 244°. *sec*-Octyl formate, b.p. 184°; acetate, b.p. 194.5°; propionate, b.p. 211°; butyrate, b.p. 220°.

**Ethers:** *n*-Octyl methyl, b.p. 75°/20 mm.; *n*-octyl ethyl, b.p. 189.2°. *sec*-Octyl methyl, b.p. 76.7°/44 mm.; *sec*-octyl ethyl, b.p. 63-65°/14 mm.

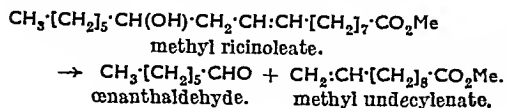
**Ketones:** Methyl *n*-octyl, m.p. 14°, b.p. 209°; ethyl *n*-octyl, b.p. 227°; di-*n*-octyl, b.p. 277°.

**Amines:** *n*-Octylamine, b.p. 175-177°. *sec*-Octylamine, b.p. 172-175°.

**Aldehyde:** *n*-Octaldehyde (octanal, capryl-aldehyde) b.p. 81°/32 mm. (semicarbazone, m.p. 101°, 2:4-dinitrophenylhydrazone, m.p. 106°).

**B. A. K.  $\alpha$ -ENANTHALDEHYDE, heptaldehyde, "enanthal"; enanthaldehyde, enanthole (U.S.A.),  $\text{CH}_3[\text{CH}_2]_5\text{CHO}$ . A colourless highly refractive liquid with a penetrating aromatic odour. B.p. 152.2-153.2°/760 mm., 59.6°/30 mm., m.p. -45°,  $\rho_4^{15}$  0.82162,  $\rho_4^{20}$  0.8495,  $n_D^{20}$  1.42571. Miscible in all proportions with alcohol and ether, slightly soluble in water, which dissolves 0.027 mol. per l. at 0°, 0.021 mol. per l. at 20°, and 0.016 mol. per l. at 40°.**

Enanthaldehyde is formed by the thermal decomposition of the sodium salt or esters of ricinoleic acid, being accompanied in the latter case by undecylenic acid or its esters. Thus methyl ricinoleate can be split almost quantitatively by dropping on to heated pumice which has been impregnated with borax, the reaction being carried out at 145 mm. (Panjutin, J. Phys. Chem. Russ. 1928, 60, 1). Enanthaldehyde (93% yield) and methyl undecylenate (87%) are obtained:



The usual method of preparation of  $\alpha$ -enanthaldehyde is by the pyrolysis of crude castor oil, which consists mainly of the glycerides of ricinoleic acid. A comprehensive study of this decomposition has been made by Barbot (Ann. Chim. 1939, [xi], 11, 519), and for maximum yield of aldehyde it is recommended that small batches of crude castor oil be distilled in as short a time as possible under reduced pressure and at a high temperature. A batch of 500 g. which was distilled in 15 minutes at over 500° and under a pressure of 12-35 mm. gave 280 g. of distillate, which on fractionation yielded 115 g.  $\alpha$ -enanthaldehyde (23%) and 66 g. undecylenic acid. In order to control frothing and the voluminous residue of polymerised products which may cause trouble during the pyrolysis, the addition of resin or "antipolymerisers" has been recommended. This method of preparation from castor oil has made  $\alpha$ -enanthaldehyde one of the most readily available of the higher aliphatic aldehydes, and it is therefore used as a starting material for the preparation of numerous heptyl derivatives.

Enanthaldehyde may be purified, if desired, through the crystalline sodium bisulphite compound in the normal manner. Crystalline derivatives for characterisation include the semicarbazone, m.p. 109°, p-nitrophenylhydrazone, m.p. 73°, and the oxime, m.p. 57-58°. The phenylhydrazone is a liquid, b.p. 202.5-203°/19 mm.

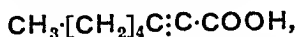
Catalytic hydrogenation yields various products, largely dependent upon the catalyst employed; with platinum black containing iron, *n*-heptyl alcohol only is obtained, but with pure platinum black some *n*-heptane is also obtained (Faillebin, *ibid.* 1925, [x], 4, 465); nickel as catalyst yields *n*-heptyl alcohol and a higher alcohol,  $\text{C}_7\text{H}_{15}\cdot\text{CH}(\text{C}_5\text{H}_{11})\cdot\text{CH}_2\cdot\text{OH}$  (see Braun and Manz, Ber. 1934, 67 [B], 1696); mixed oxides of nickel, copper, and cobalt give *n*-heptyl alcohol and diheptyl ether (Riedel, G.P. 444665); vapour-phase hydrogenation at atmospheric pressure with a nickel catalyst leads to a degradation, *n*-hexane being the chief product (Suen and Fan, J. Amer. Chem. Soc. 1942, 64, 1460). In the presence of ammonia, hydrogenation with nickel at atmospheric pressure yields *n*-heptylamine and with colloidal platinum, di-*n*-heptylamine is produced (Skita and Keil, Ber. 1928, 61 [B], 1456).

Reduction of  $\alpha$ -enanthaldehyde with iron and acetic acid gives *n*-heptyl alcohol in 80% yield (Organic Syntheses, 1941, Coll. Vol. I, 304). The alcohol has also been obtained by using zinc and acetic acid, sodium amalgam and acetic acid, and by electrolytic reduction. If added to fermenting sugar solution, the aldehyde is reduced biochemically to the alcohol.

Oxidation of  $\alpha$ -enanthaldehyde to *n*-heptic acid ( $\alpha$ -enanthic acid) occurs readily with acidic permanganate (*ibid.* 1943, Coll. Vol. II, p. 315).

Treatment of  $\alpha$ -enanthaldehyde with hydroxylamine hydrochloride and sodium carbonate gives  $\alpha$ -enanthaldoxime (*ibid.*, p. 313), which can readily be converted into *n*-heptylamine by reduction with sodium and alcohol (*ibid.*, p. 318). Treatment of the oxime with aluminium oxide at 340-360° yields *n*-heptonitrile.

With phosphorus pentachloride, cœnanthaldehyde gives chiefly 1:1-dichloroheptane,  $\text{CH}_3[\text{CH}_2]_5\text{CHCl}_2$ , which may be converted into heptyne-1,  $\text{CH}_3[\text{CH}_2]_4\text{C}\equiv\text{CH}$  by means of sodamide (Bourguet, Compt. rend. 1923, 177, 823), so that this is one of the most readily obtainable of the higher acetylenes. Treatment of the sodium salt of heptyne-1 with carbon dioxide leads to the acetylenic acid



the methyl ester of which is an artificial violet perfume, usually described as "methyl heptino carbonate."

B. A. K.

**ÆNIDIN** is the anthocyanidin obtained by the acid hydrolysis of cœnin. It is identical with malvidin.

W. B.

**ÆNIN.** The colouring matter of the skins of dark blue wine grapes (*Vitis vinifera* L.) was first obtained in a pure condition by Willstätter and Zollinger (Annalen, 1915, 408, 83). The fresh skins of North Italian grapes were extracted by means of glacial acetic acid, and the crude colouring matter was precipitated from the deep red solution by adding ether. It was converted into the *picrate*, which crystallised readily, and again into the *chloride*. Crystallisation by allowing a solution in a mixture of methyl and ethyl alcohols containing hydrogen chloride to evaporated slowly gave the chloride,  $\text{C}_{23}\text{H}_{25}\text{O}_{12}\text{Cl}$ , in the form of dark red or brownish-red, thick prisms with a beetle green lustre, containing from 4 to 6  $\text{H}_2\text{O}$ . Robinson, Levy, and Posternak (J.C.S. 1931, 2701) have defined the best conditions for the crystallisation of cœnin chloride. The crude chloride is dissolved in very dilute methyl-alcoholic hydrogen chloride, the concentration of the acid is increased, and almost at once the chloride is precipitated by adding ether. It is dissolved in 1% methyl-alcoholic hydrogen chloride, the solution is filtered, and the acid content of the filtrate increased to 4-5%. The chloride, which crystallises with a marked yellow sheen, is quite free from accompanying anthocyanidin and, when dried in air, consists of a *trihydrate*.

The *chloride* is easily soluble in cold water. A hot dilute solution is initially brownish-red, but the colour changes to violet and then fades because of the successive formation of *colour-base* and *pseudo-base*. In the presence of acid, even 0.2% tartaric acid, aqueous cœnin solutions are stable. It is more readily soluble in dilute hydrochloric acid than is delphinin (v. Vol. III, 555c); it dissolves very easily in 2%, and is still appreciably soluble in 5% acid, though in 10% it is only sparingly soluble, and in 20% almost insoluble. Sodium carbonate added to an acidified aqueous solution gives a blue-violet to violet-blue colour, which is stable on dilution and unchanged on the further addition of sodium hydroxide. Lead acetate gives a dark blue and copper sulphate a violet precipitate. When ferric chloride is added to an aqueous solution the colour deepens but there is no other change. Tannin causes an aqueous solution to become bluer and more intense. In alcohol,

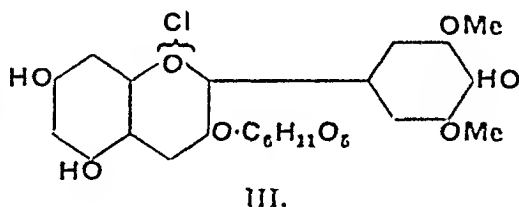
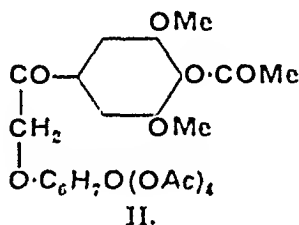
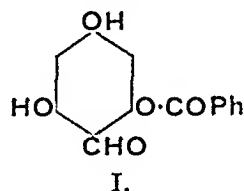
cœnin dissolves with a red-violet colour which is tinged violet.

Ænin is strongly laevorotatory

$$([\text{M}]_{627} = -2,867, [\text{M}]_c = -2,227).$$

In dilute acids it shows a broad absorption band, which does not extend so far into the blue as does that of cyanin. In its distribution between aqueous acid and isoamyl alcohol cœnin resembles idæin (v. Vol. VI, 411a).

Boiling for a few minutes with concentrated hydrochloric acid hydrolyses cœnin to equimolecular proportions of glucose and "œnidin" (identical with malvidin, v. Vol. VII, 482a), which is a dimethyl ether of delphinidin. Cœnin has been synthesised by Robinson *et al.* (l.c.) who condensed 2-O-benzoylphloroglucinaldehyde (I) with  $\omega$ -O-tetra-acetyl- $\beta$ -glucosidoxy-4-acetoxy-3:5-dimethoxyacetophenone (II) by means of hydrogen chloride in dry ethyl acetate. An acetylated flavylum salt was obtained which gave cœnin (III) after treatment first with sodium hydroxide and then with hydrochloric acid.



In certain varieties of hothouse grapes cœnin is accompanied by about 10% of malvidin, whilst in red wine as much as one quarter of the colouring matter may consist of the free anthocyanidin.

"Cyclamin" isolated from the flowers of *Cyclamen persicum* Mill. is identical with cœnin (Bell and Robinson, J.C.S. 1934, 136, 813), which is also the main constituent of the pigment obtained from the red flowers of *Primula polyanthus* (Scott-Moncrieff, Biochem. J. 1930, 24, 767).

"Ampelopsin" (v. Vol. I, 357b; III, 554c), too, the colouring matter of the berries of the wild vine (*Ampelopsis quinquefolia* Michx.) probably consists largely of cœnin.

W. B.

**ÆSTRIOL** (v. Vol. VI, 269a).

"OILDAG" (v. Vol. I, 119d; II, 310b; III, 288a).

## OILS, DRYING (c. Vol. IV, 81c).

**OILS, ESSENTIAL.** Essential oils may be broadly defined as mixtures of volatile organic compounds, non-miscible with water, to which the odours of vegetable substances are due. They consist mainly of terpenes and their oxygenated derivatives but occasionally contain compounds of nitrogen and sulphur; other elements are not known to be present. The essential oils may occur as such in plants or, less frequently, may result from the degradation of glycerides by enzyme action. The chief constituents are:

**Hydrocarbons.**—Ocimene, myrcene, eymene, pinene, sylvestrene, limonene (dipentene), camphene, phellandrene, fenchene, geraniolene, eudesmol, caryophyllene, santalenes.

**Alcohols.**—Geraniol, nerol, citronellol, terpineols, borneol, linalool, menthol, santalol, isopulegol, perillyl alcohol, fenchyl alcohol, cedrol, farnesol, phenylethyl, benzyl, cinnamyl, and methyl alcohols.

**Phenols.**—Thymol, carvacrol, eugenol, vanillin.

**Ethers.**—Anethol, methyl chavicol, saffrole, eucalyptol, ascaridole.

**Aldehydes.**—Citral, citronellal, anisaldehyde, benzaldehyde, cinnamaldehyde.

**Ketones.**—Camphor, irone, carvone, menthone, pulegone, fenchone, piperitone, acetophenone.

**Esters** of acetic, butyric, tiglic, salicylic, benzoic acids.

## METHODS OF EXTRACTION.

There are, in general, four methods of extraction:

1. Distillation with steam or water.
2. Expression.
3. Extraction by means of volatile solvents.
4. Absorption in purified fats (*Enfleurage*).

By far the greater number of essential oils are isolated by distillation at atmospheric pressure with steam or water. The methods are comprehensively treated by T. H. Durraus (*Perf. & Essent. Oil Rec.*, June 8, 1920) in C. Riechenberg, "Einfache und fraktionierte Destillation in Theorie und Praxis," 1923, by A. L. Bloomfield (*Perf. & Essent. Oil Rec.*, March 24, 1936 *et seq.*) and in S. Young, "Distillation Principles and Processes," Macmillan, 1922. This method which dates back to remote antiquity is applied throughout the world to a wide variety of vegetable materials. It consists essentially in treating the plants in a suitable state of division to the action of steam generated either in a separate boiler or in the still itself by direct heat in the presence of water. Frequently, distillation is carried out without any pretreatment of the vegetable material, as in the case of easily permeable materials such as leaves, twigs, petals, flowers, bnds, herbs, and grasses, but occasionally it has to be reduced to a suitable state of subdivision in order to render it permeable and thus permit the distillation to be completed within a reasonable time. The speed of distillation may be increased by working the still under pressure and by the use of superheated steam, but these devices are only employed when the higher temperatures thus obtained do not cause undesirable decomposition. Experience has shown that a preliminary partial

drying of the materials sometimes aids subsequent distillation and better products are in consequence obtained, but there is considerable risk of loss of essential oil by evaporation and by aerial oxidation. In some instances, such as Patchouli, fermentation is permitted before distillation in order to rupture the oil cells, while in the case of kernels such as bitter almonds, apricots, and peaches, enzymic fermentation is first necessary in order to liberate the benzaldehyde from the glucoside amygdalin.

The proportion of oil which passes over with the steam depends on three factors—the vapour pressure and the molecular weights of its constituents and the rate at which the oil is liberated from the charge. The following table indicates the *average* oil percentages in such distillates, but the results are largely dependent on the last factor.

Material.	% Oil.
Ajowan seeds . . . . .	0.77
Angelica seeds . . . . .	0.2
Aniseeds . . . . .	0.8-1.2
Bay leaves . . . . .	0.76
Cedarwood . . . . .	1-1.4
Cubebs . . . . .	1.2
Ginger root . . . . .	0.3
Coriander seeds . . . . .	0.56
Caraway seeds . . . . .	2.2-3
Cloves . . . . .	0.6-0.9
Patchouli leaves . . . . .	0.12
Peppermint . . . . .	0.1
Pimento . . . . .	0.18
West Indian Sandalwood . . . . .	0.2-0.34
Celery seeds . . . . .	0.17
Vetiver root . . . . .	0.02
Cinnamon bark . . . . .	0.32
(Rechenberg, <i>op. cit.</i> )	

When reading the above table it must be borne in mind that during the initial stages of the distillation, when the distillate consists largely of the constituents of lower boiling-point, the percentage may be very much higher while the reverse may be the case towards the end of the distillation; indeed, the percentage may then be unprofitably low.

Distillation is not a suitable process for the isolation of certain essential oils which undergo some destruction on exposure to heat and water, and in such cases one of the three other methods mentioned above are used. Citrus oils, lemon, orange, bergamot, and grapefruit are prepared mainly by expression, the Sicilian Scorzetta and Spunga (Sponge) method in particular being used for the preparation of oil of lemon. This method is described by A. H. Bennett (*Chem. and Ind.* 1943, 320) as follows:

"The fruit is cut in half and the pulp separated from the peel by means of a special form of spoon with a sharp edge. This is inserted at the junction of the white pith (albedo) with the juice-containing pulp, and by a quick turn of the wrist this pulp is extracted whole, without any liberation of juice, leaving the peel practically free from adhering pulp. The peel is dipped in water and allowed to stand for some hours and then passes to the workman who extracts the oil. This is done by pressing the peel between sponges. The bending of the peel breaks the oil cells and the oil, together with some water, spurts out and the mixture is collected in an earthenware bowl from which the oil is decanted at the end of the operation. Absorption by the



sponge breaks any emulsion that may have been formed by the colloidal substances present in the water and the decanted oil is almost clear."

In California the whole fruit is crushed, the juice containing about 1% of oil is screened to remove coarse particles and the oil separated by a centrifuge of the high-speed clarifier type. Complete separation of the oil is not effected by this method, about one-half remaining in the juice from which an oil of inferior quality may be isolated by distillation.

In another method the whole fruit is rasped by a revolving surface having sharp points which scrape the fruit while being sprayed with water containing 2% of sodium bicarbonate (U.S.P. 1814888, 1931). The oil is then centrifuged out and the clear oil thus obtained is almost equal in quality to the hand-pressed oil. Recently, the "sfumatrice" machine has been employed. In this machine the depulped peel is subjected to a bending process mechanically while being sprayed with water, the object being to disrupt the oil cells and liberate the oil without other material which causes emulsification. Orange oil is mainly obtained by the sponge method in Sicily and by the rasping method in California and Rhodesia.

Bergamot oil is separated mechanically by rasping the whole fruit between two cup-shaped surfaces, the upper one of which is ribbed and rotates while the lower is stationary and provided with a grating surface. The resulting mixture is pressed in sacks to remove the solid raspings and the oil and water are subsequently separated from one another.

Extraction by volatile solvents is resorted to, mainly in the Grasse district of South France, for the extraction of flower perfumes such as Hyacinth, Tuberose, Jasmine, Nareissus, as the delicate odour of these oils is spoilt by steam distillation methods. A petroleum fraction of very low boiling range is the usual solvent as it has the advantage that it does not extract water or too large a proportion of non-volatile substances such as chlorophyll, stearoptene, resins, and waxes; such extracts are termed "Concretes," and are usually of a thin cheese-like consistency. Re-extraction of the Concrete with cold alcohol yields, after evaporating the alcohol, the so-called "absolute" flower perfume and consists mainly of the essential oil.

The enfleurage process consists in exposing flower blossoms for several days on sheets of purified lard cast on glass; the lard absorbs the volatile essential oil, which is then extracted with cold alcohol as above.

## ANALYSIS.

The characteristics quoted in this monograph for the various essential oils are those usually found, and it does not follow that oils which do not conform with these figures are adulterated. Quite large variations in the composition of oils may be the result of climatic conditions, environment, soil composition, history of the crop, time of cropping, age, method of distillation, and so on, while not infrequently variations are caused by the admixture or confusion of two species

of the plants such as often occurs with the lavenders, pine needles, and eucalypts.

Information of great value can generally be obtained by carefully smelling the oil as it evaporates from a clean filter paper. By this means an expert can often form a valid conclusion on the quality and purity of an oil, whereas reliance on analytical figures alone may be quite misleading.

Although blending is frequently done, adulteration is not widely practised now, but was common, and even condoned, a decade or so ago; thus the adulteration of Ceylon citronella oil with paraffin and of cassia oil with rosin were recognised trade practices. Other forms of adulteration which have been frequently recorded are lemon oil with citral and terpene from the preparation of terpeneless oil; otto of rose with citronellol and waxes; bitter almond oil with synthetic benzaldehyde; cinnamon oil with synthetic cinnamaldehyde; wintergreen oil with synthetic methyl salicylate; American peppermint oil with rectified Japanese oil; lavender and bergamot oils with linalyl and terpinyl acetates and synthetic esters such as triethyl citrate; sandalwood oil with cedar wood oil; and neroli oil with petitgrain oil.

Methods for determining the characteristics of essential oils have been recommended by the "Standing Committee on the Uniformity of Analytical Methods" first published in "The Analyst" (1927 *et seq.*). (See also F. W. Atack and E. Hope, "The Chemists' Year Book," 1936, Sherrat and Hughes, Manchester.) The conditions recommended for the determination of the physical characteristics are as follows:

**Specific Gravity ( $\rho$ ).**—Temperature (unless otherwise stated) 15.5°C. compared with water at 15.5°C. (The coefficient of expansion of essential oils is of the order of 0.001 per °C.)

**Optical Rotation ( $\alpha$ )** is expressed in terms of angular rotation of sodium light passing through 100 mm. of oil at 20°C.

**Refractive Index ( $n_D$ )** is usually determined in an Abbé type refractometer at a temperature of 20°C. (unless otherwise stated) for the D sodium line. (The refractive index diminishes by about 0.00015 per 1°C. rise in temperature.)

**Solubility in Alcohol.**—1 c.c. of the oil is shaken in a 100 c.c. stoppered graduated glass cylinder with alcohol at 15°C. of definite strength, 1 c.c. of alcohol being added repeatedly until a clear solution is first obtained. The test is not always definite as permanent opalescence sometimes obscures the end-point.

**Melting- and Freezing-Points (M.p. and F.p.).**—The apparatus recommended consists of a stout-walled glass test-tube, 125×15 mm. (inside measurements), fitted into a wide-mouthed jar or bottle of about 500 c.c. capacity, by means of a bored cork and an inner test-tube, 100×21 mm., fitted into the larger tube also by means of a bored cork. The thermometer used should be readable to one-fifth of a degree, and should have a diameter about 5 or 6 mm., and the length of the bulb should be between 15 and 20 mm.

**Freezing-Points: Method of Procedure.**—In order to obtain a preliminary indication, a few c.c. of the oil are cooled in a small test tube and

stirred with the thermometer until solidification takes place; the temperature is noted, and the tube of solidified oil set aside in a cool place. The outer container of the apparatus is then filled with water (or brine) at a temperature about five degrees lower than that indicated above and the larger outer tube fitted in its place. Into the inner tube 100 c.c. of the oil are placed, the thermometer inserted, and the tube and oil cooled to the temperature indicated in the preliminary test. The tube and contents are now inserted in the apparatus, and the temperature allowed to fall a further one or two degrees. The oil is then seeded with a trace of the previously solidified oil and stirred with the thermometer until solidification takes place. The highest temperature reached is taken as the freezing-point.

*Melting-Points.*—After the determination of the freezing-point the inner and outer tubes are removed together from the water-jacket and the temperature allowed to rise slowly, the oil being stirred continuously with the thermometer until the liquid becomes "clear."

#### ESTIMATION OF CONSTITUENTS.

The following methods are those recommended for the estimation of various compounds in essential oils, as the methods are not in general specific it is usual to return the results in terms of the preponderating member of the class.

##### Esters.

The following reagents are required:

Alcohol (90% by volume).

Alcoholic potassium hydroxide: approximately  $N/10$  prepared by diluting alcoholic potassium hydroxide, approximately  $N/2$ , with 90% (by volume) alcohol and standardising by titration with  $N/10$  acid using phenolphthalein as indicator.

Alcoholic potassium hydroxide: approximately  $N/2$  prepared by dissolving 33 g. of potassium hydroxide of reagent purity in 1 l. of 95% (by volume) alcohol, allowing to stand, and decanting or filtering the clear liquid.

Sulphuric acid or hydrochloric acid:  $N/2$ .

Phenolphthalein: 0.2% solution in 60% alcohol.

*Method of Determination.*—Two grams of the oil, or other suitable quantity so that the amount of alkali added is at least double that required for saponification, are weighed into the saponification flask; 5 c.c. of freshly well-boiled and neutralised alcohol are added, and the free acid is titrated with  $N/10$  alcoholic potassium hydroxide solution, using 0.2 c.c. of phenolphthalein solution as indicator. The result of the titration is calculated to acid value (mg. of KOH required for the neutralisation of 1 g. of the oil). To the neutralised solution in the flask are then added 20 c.c. of  $N/2$  alcoholic potassium hydroxide solution, and the whole is boiled under a reflux condenser for 1 hour, at the end of which time the excess of alkali is titrated immediately with  $N/2$  acid, using an additional 0.5 c.c. of phenolphthalein solution as indicator. At the same time a blank determination is carried out by boiling for 1 hour under a reflux condenser 5 c.c. of alcohol, 20 c.c. of

$N/2$  alcoholic potassium hydroxide, and 0.2 ml. of phenolphthalein solution, then titrating immediately with  $N/2$  acid after the addition of a further 0.5 c.c. of phenolphthalein solution.

The difference between the two titrations is calculated to the percentage of esters in the usual manner, using the appropriate factor. Those for the most commonly occurring esters are as follows:

Bornyl acetate . . . 0.0981	Santalyl acetate . . . 0.1311
Geranyl acetate . . . 0.0981	Methyl salicylate . . . 0.0760
Linalyl acetate . . . 0.0981	Geranyl tiglate . . . 0.1181
Menthyl acetate . . . 0.0991	

##### Alcohols. (Acetylatale Constituents.)

Alcohols such as geraniol, citronellol, menthol, and linalool are estimated by acetylating the oil and then determining the ester content. The method of acetylation is as follows:

10 c.c. of the oil, 20 c.c. of acetic anhydride (95–100%), and 2 g. of freshly fused anhydrous sodium acetate, are mixed in a long-necked round-bottomed 200 c.c. Kjeldahl flask; a fragment of broken glass is added, and the contents boiled gently under an air reflux condenser for 2 hours.

The flask should be supported on a sheet of asbestos board, in which has been cut a hole about  $1\frac{1}{2}$  in. in diameter, and should be heated by a small naked flame, placed about 1 in. below, and not impinging on the bottom of the flask.

At the expiration of 2 hours, the flame is removed and the flask allowed to cool: 50 c.c. of water are added, and the flask and contents heated on a boiling water bath for 15 minutes, with frequent and thorough shaking. After cooling, the contents of the flask are transferred to a separating funnel and the lower aqueous layer rejected. The acetylated oil is then washed successively with: (1) 50 c.c. of brine (saturated aqueous solution of sodium chloride); (2) 50 c.c. of brine containing 1 g. of sodium carbonate in solution; (3) 50 c.c. of brine; (4) 20 c.c. of water. Mixtures 1, 2, and 3 should be shaken vigorously, but the final washing with water must be conducted with gentle shaking only.

The oil is separated and mixed with about 3 g. of powdered anhydrous sodium sulphate, stirred for 15 minutes or until one drop produces no cloudiness when added to 10 drops of carbon disulphide in a dry test tube. The oil is then filtered through a dry filter paper in a covered funnel and the esters determined as above.

Certain oils, such as citronella, contain the aldehyde citronellal, which, under the action of acetic anhydride, isomerises to the ring alcohol isopulegol, the alcohol value being raised correspondingly. In such cases it is usual to return the result as "total acetylatale constituents," calculated as geraniol.

To differentiate between the geraniol and the citronellal of Java citronella oils, the aldehyde is converted into the unsaponifiable nitrile, and the alcohols re-estimated. The procedure is as follows:

10 g. of hydroxylamine hydrochloride is dissolved in 25 c.c. of water, and a solution of 10 g. potassium carbonate in 25 c.c. of water added; the mixture is filtered and shaken thoroughly with about 10 g. of the oil for 2 hours at 15–18°.

and titrate with the N./2 alcoholic potassium hydroxide until the red colour changes to yellow. Continue the shaking and titrating until the full yellow colour of the indicator is permanent in the lower layer after shaking vigorously for 2 minutes, and then allowing to stand to separate. The reaction is slow towards the end, but should be complete in about 15 minutes.

The completed titration liquid, plus a slight excess of alcoholic potassium hydroxide (1 or 2 drops), may be used as colour standard for the end-point of a subsequent determination.

The number of c.c. of N./2 alcoholic potassium hydroxide required, multiplied by the correcting factor 1.008, by the factor 0.076 for citral, and by 100, and divided by the weight of the oil taken, will give the percentage of aldehydes, calculated as citral.

The volume of the N./2 hydroxylamine hydrochloride used should be varied according to the citral content of the oil, the excess of hydroxylamine hydrochloride over the alcoholic potash required being from 1 c.c. to 2 c.c. in all cases.

**Sulphite Method.**—Suitable for oils of almond, cassia, cinnamon bark, and lemongrass, but not considered to be so accurate as the hydroxylamine method given above.

10 c.c. of the oil is accurately pipetted into a flask of 150 c.c. capacity, the neck of which is long and about 10 mm. internal diameter, 10 c.c. of which is graduated in 0.1 c.c. (Cassia flask). To this is added about an equal volume of hot sodium bisulphite solution (30% strength) and the mixture well shaken for a few minutes; frequently, however, the mixture becomes solid almost immediately, and further quantities of bisulphite solution are added from time to time with frequent shaking, and the whole is kept hot on a boiling-water bath until the solid first formed is completely dissolved and only oil remains; the flask is then filled with bisulphite solution, so as to bring the unabsorbed oil up into the graduated portion of the neck; it is then set aside to cool and for the unabsorbed oil to float out. The difference between the original volume of the oil and that unabsorbed is a measure by volume of the aldehyde content of the oil.

#### Ketones.

In oils of Caraway, Dill, Spearmint, Peppermint, Pennyroyal, and *Eucalyptus dives*.

The solutions required are the same as those for Citronellal with the exception that the alcoholic potassium hydroxide must be N./1.

**Method of Determination.**—Weigh out exactly into a stoppered tube (approximately 150 mm. long by 25 mm. in diameter) about 1.5 g. of caraway, dill, or spearmint oil, or 3 g. of peppermint oil; add 20 c.c. of the N.-hydroxylamine hydrochloride reagent, and titrate with N.-alcoholic potassium hydroxide until the red colour changes to yellow. Place the tube in a water-bath at 75–80°, and neutralise the liberated acid with N.-alcoholic potassium hydroxide at five-minute intervals; at the expiration of 40 minutes complete the titration to the full yellow colour of the indicator and note the reading of the burette.

Two determinations should be carried out

side by side, using two burettes, and the one first completed, plus a slight excess of alcoholic potassium hydroxide (0.5 c.c.), should be used as a colour standard for the end-point of the duplicate. The percentage should be calculated from the duplicate determination.

The number of c.c. of N.-alcoholic potash required, multiplied by the correcting factor 1.008, by the factor 0.150 for carvone or 0.154 for menthone, and by 100, and divided by the weight of oil taken will give the percentage (by weight) of the ketones calculated as carvone or as menthone.

For the estimation of pulegone in Pennyroyal oil a reaction time of 75 minutes is required.

#### Phenols.

In oils of Ajowan, Bay, Cinnamon leaf, Clove, Origanum, Pimento, and Thyme.

The determination is carried out in a flask consisting of a bulb of about 150 c.c. capacity with a long neck, of which 10 c.c. is graduated in tenths of a cubic centimetre, the length of the graduated portion being not less than 15 cm. Before use, the flasks should be cleansed with concentrated sulphuric acid and well rinsed out with distilled water.

**Method of Determination.**—80 c.c. of 5% aqueous potassium hydroxide solution are placed in the flask, followed by 10 c.c. of the clear oil, and the mixture thoroughly shaken at 5 minute intervals during 30 minutes, at room temperature.

The unabsorbed portion of the oil should then be raised into the neck of the flask by the gradual addition of more of the potassium hydroxide solution, and the separation of the oily layer facilitated by rotating the flask between the hands and gently tapping. After standing for not less than 24 hours, the volume of unabsorbed oil should be read off, taking the bottom line of the meniscus, in each case. The proportion absorbed, multiplied by 10, will give the percentage by volume of the phenolic content of the oil under examination.

**Eucalyptol (Cineole).**—In oils of Cajuput, Eucalyptus, Camphor containing a minimum of 50% of cineole.

Three grams of oil and 2.1 g. of pure o-cresol are accurately weighed into a test tube of about 15 mm. diameter and 80 mm. length; the mixture is carefully melted while stirring with an accurate thermometer graduated in fifths of a degree centigrade; when the mixture is completely homogeneous stirring is stopped and the test tube is inserted through a bored cork into a wide-mouthed bottle acting as an air jacket and allowed to cool slowly until crystallisation commences. The mixture is then stirred vigorously and the highest temperature reached is taken as the freezing-point. The mixture is remelted and the determination repeated until two concordant results are obtained. The percentage of cineole is calculated from the following Table:

% Cineole.	F.p. °o.	% Cineole.	F.p. °o.
100	55.2	70	41.7
95	53.5	65	38.8
90	51.5	60	35.0
85	49.5	55	31.2
80	47.0	50	27.4
75	44.4	45	23.5

For oils of cineole content below 50% it is advisable to add a known proportion of pure cineole before making the determination.

### Oil of Ajowan.

**Source.**—Fruit of *Ptychotis ajowan* (*Carum copticum*). (*Trachyspermum ammi*) (Bishops weed). Yield up to 4%.

**Habitat.**—India.

**Constituents.**—Thymol 35-55%, carvacrol, cymene, pinene, dipentene, terpinene, phellandrene.

**Characteristics.**— $\rho$  0.91-0.93;  $\alpha$  0° to +2°;  $n_D$  1.485-1.510.

**Uses.**—Carminative, antiseptic. Dose  $\frac{1}{2}$ -3 mins.

### Oil of Bitter Almond.

(*Oleum Amygdalæ Amaræ*.)

**Source.**—Fermented kernels of *Prunus amygdalus* (almond). (*Amygdalus communis*.) *P. persica* (peach). *P. armeniaca* (apricot). Yield up to 1.6%.

**Habitat.**—World-wide in temperate and tropical climes.

**Isolation.**—The kernels are crushed, the fixed glyceride oil pressed out, and the press cake finely ground; then mixed with water and maintained at a temperature approaching 60° to cause enzymic splitting of the benzaldehyde cyanohydrin. The benzaldehyde is isolated by steam distillation, care being taken to lead the poisonous hydrocyanic acid away. The S.A.P. (sine acido Prussico) quality is obtained by washing the oil with ferrous sulphate—lime solution.

**Constituents.**—Benzaldehyde 96-98%.

**Characteristics.**—S.A.P. oil.  $\rho$  1.050-1.055;  $\alpha$  up to +10°;  $n_D$  1.542-1.546.

**Uses.**—Flavouring and perfumery.

### Oil of Aniseed.

(See also Star Aniseed.)

**Source.**—Fruit of *Pimpinella anisum*. Yield up to 6%.

**Habitat.**—Asia Minor and S. Russia.

**Constituents.**—Anethole 80-95%, fenchone, cymene, anisole, anisaldehyde, cuminaldehyde.

**Characteristics.**— $\rho$  20° 0.975-0.990;  $\alpha$  0 to -2°;  $n_D$  1.552-1.560. Soluble in 3 vol. 90% alcohol. F.p. 15-19°. The B.P. recognises both oils of Aniseed and requires  $\rho^{20}$  0.980-0.994;  $\alpha$  -2 to +1;  $n_D$  1.553-1.560. F.p. 15° min. M.p. 17° min. Soluble in 3 vol. of 90% alcohol.

**Uses.**—Medicinally as an aromatic carminative and expectorant for linctus; also for the treatment of cholera. Dose 1-3 mins. In Pharmacy for Elixir of Cascara Sagrada and Tinct. Opii. Camphorata. Flavouring confectionary, liquours, and dentifrices. An inferior oil is distilled from the leaves. Star Aniseed is the usual aniseed oil of commerce.

### Oil of Bay.

(*Oleum Myrciæ*.)

**Source.**—Leaves of *Pimenta acris* tree (*Eugenia acris*) (*Myrcia acris*). Yield up to 3%.

**Habitat.**—West Indies; Venezuela.

**Constituents.**—Eugenol, methyl eugenol, chavicol, methyl chavicol, citral, myrcene, phellandrene, pinene.

**Characteristics.**— $\rho$  0.960-0.985;  $\alpha$  up to -3°;  $n_D$  1.50-1.52. Phenols 50-70%. Soluble in 2 vol. 70% alcohol.

**Uses.**—Bay Rum and astringent lotions. R.W. Coefficient, 5.5.

### Oil of Bergamot.

**Source.**—Fresh peel of *Citrus bergamia* (*aurantium*).

**Habitat.**—South Italy.

**Constituents.**—Linalool, linalyl acetate, nerol, terpinol, dihydrocymic alcohol, octylene, pinene, camphene, limonene, bornylene, bisabolene, bergaptene.

**Characteristics.**— $\rho$  0.878-0.887;  $\alpha$  +5 to +25°;  $n_D$  1.464-1.468. Linalyl acetate 30-45% (usually 35-40%). Linalool 18-40%. Stearoptene 4.2-6.2%. Soluble in 2 vol. 80% alcohol.

**Uses.**—Widely in perfumery, especially for Eau de Cologne. For methods of detecting esters added to give fictitious values, see Perf. & Essent. Oil Rec. 1923, 14, 359.

### Oil of Cajuput.

**Source.**—Leaves and twigs of *Melaleuca shrubs*, especially *M. maideni* (*M. leucadendron*; *M. minor*). Yield up to 2%.

**Habitat.**—Malay peninsula; Dutch East Indies; North Australia; Strait Settlements; Molucca Isles.

**Constituents.**—Cineole, 1- $\alpha$ -pinene, 1-limonene, terpinol, terpinyl acetate and butyrate, benzaldehyde, sesquiterpenes.

**Characteristics.**— $\rho$  0.917-0.930;  $\alpha$  -1° to -5°;  $n_D$  1.465-1.472. Cineole 45-65%. Soluble in 2 vol. 80% alcohol. The B.P. requires:  $\rho$  0.916-0.926;  $\alpha$  not over -4°;  $n_D$  1.464-1.472. Cineole 50-65%. Soluble in 2 vol. 80% alcohol.

**Uses.**—Medicinally as an antispasmodic carminative and intestinal antiseptic. R.W. Coefficient, 1; Mild external counter-irritant for rheumatism. Dose 1-3 mins.

### Oil of Cananga.

**Source.**—Flowers of *Cananga odorata*. Yield up to 2%.

**Habitat.**—Java and Manila; also to a small extent in Reunion, Seychelles, and Madagascar.

**Constituents.**—*p*-Cresyl methyl ether with small amounts of nerol, farnesol, linalool, linalyl acetate, and sesquiterpenes.

**Characteristics.**—Java Cananga:  $\rho$  0.91-0.92;  $\alpha$  -15° to -40°;  $n_D$  1.495-1.505. Ester value 10-30. Acetyl value 50-80. An oil of superior odour obtained in Manila by selection of the choicest fractions from the distillation is known as Ylang-ylang.

**Uses.**—Perfumery.

### Oil of Camphor.

**Source.**—*Cinnamomum camphora*. (*Laurus camphora*.) Yield: Leaves and twigs 1-4½%. Trunk and branches up to 6%.

**Habitat.**—Japan, Formosa, Hainan, and East Central China.

**Constituents.**—The leaves and small twigs yield an oil consisting mainly of camphor, while the oil from the trunk and large branches contains little or no camphor and consists largely of safrole; the other constituents are cineole, terpenes, and sesquiterpenes. Camphor (up to 40%) and Safrole are isolated from the oil by freezing and fractionation respectively and the residual oils are sold as Light and Heavy Camphor Oils.

**Characteristics.**—(i) *Light or White Camphor Oil.*  $\rho$  0.87–0.92;  $\alpha$  +9° to +23°;  $n_D$  1.465–1.475. Boiling range 165–215°. R.W. Coefficient, 0.4. This oil consists mainly of pinene, fenchene, limonene, phellandrene, cineole, with small proportions of terpineol, borneol, terpineol, citronellol, cuminol, carveol, eugenol, 4-ethylguaiaacol, piperitone, etc.

(ii) *Heavy or Brown Camphor Oil.*— $\rho$  0.97–1.07;  $n_D$  1.49–1.53. Boiling range 200–270°. This oil has had most of the safrole removed, but oils containing 25–35% of safrole have  $\rho$  1.018–1.028. The constituents of the desafroled oil are mainly sesquiterpenes such as cadinene,  $\alpha$ - and  $\beta$ -camphorene. Both light and heavy camphor oils vary widely in quality.

**Uses.**—Camphor is used medicinally and for the manufacture of celluloid. Safrole is used for the manufacture of heliotropin and as a perfume for household soaps; light camphor oil for the isolation of cineole, as a substitute for turpentine and for liniments; heavy camphor oil for liniments and as a basis-perfume for soap stock.

#### Oil of Caraway.

**Source.**—Seeds of *Carum carvi*. Yield 3–7%.

**Habitat.**—Northern and Central Europe, mainly Russia, Poland, and Holland.

**Constituents.**—Carvone 50–65%, limonene, traces of dihydrocarvone, carveol, and dihydrocarveol.

**Characteristics.**— $\rho$  0.91–0.92;  $\alpha$  +69° to +82°;  $n_D$  1.484–1.490. The B.P. requires:  $\rho$  0.91–0.92;  $\alpha$  +70° to +80°;  $n_D$  1.485–1.492. Soluble in 1 vol. 90% or 7 vol. 80% alcohol. Carvone 53–63%.

**Uses.**—Medicinally, as an aromatic carminative to relieve colic and griping, especially for children, in the form of Aqua Cari. Dose 1–3 mins. Perfumery and flavouring.

#### Oil of Cassia.

**Source.**—Bark, leaves, and twigs of *Cinnamomum cassia* (Chinese Cinnamon). Yield up to 2%.

**Habitat.**—Kwangsi and Kwantung provinces, China.

**Constituents.**—Mainly cinnamaldehyde, also *o*-methoxycinnamaldehyde, *o*-coumaraldehyde, salicylaldehyde, benzaldehyde, cinnamyl alcohol, coumarin.

**Characteristics.**— $\rho$  1.05–1.07;  $\alpha$  -1° to +6°;  $n_D$  1.60–1.61. Aldehydes 80–95%. Soluble in 2 vol. 70% alcohol. Formerly often adulterated with rosin and paraffin. Lead sometimes present.

**Uses.**—Flavouring. Soap perfumery. Isolation of cinnamaldehyde. R.W. Coefficient, 1.4. Medicinally as for cinnamon oil. Dose  $\frac{1}{2}$ –3 mins.

#### Oil of Cedarwood.

**Source.**—*Juniperus virginiana* (Virginia Cedar, Florida Cedar). Mainly from the waste shavings of pencil factories; also, to a small extent, from *Cedrus atlantica*, *Cedrus libani*, *Juniperus procera* and other varieties. Yield up to 5%.

**Habitat.**—Widely in U.S.A.

**Constituents.**—The sesquiterpenes—cedrol, cedrenol, cedrene.

**Characteristics.**—Oil from *J. virginiana*.  $\rho$  0.94–0.97;  $\alpha$  -25°–60°;  $n_D$  1.49–1.52. Ester value 2–7. Acetyl value 15–50. Soluble in 20 vol. 90% alcohol.

**Uses.**—Incense and fumigating. R.W. Coefficient, 1.6. Soap perfumery. Microscopy.

#### Oil of Chamomile.

(*Oleum Anthemidis*.)

**Source.**—Flowers of *Anthemis nobilis* (Roman chamomile). Yield up to 1%.

**Habitat.**—Southern and Western Europe. Britain, Belgium, France, Italy.

**Constituents.**—Mainly esters of butyric, angelic, and tiglic acid with amyl and hexyl alcohols; also anthemol and azulene, to which the blue colour of the oil is due.

**Characteristics.**— $\rho$  0.905–0.920;  $\alpha$  -3° to +3°;  $n_D$  1.442–1.459. Ester value 220–320.

**Uses.**—Medicinally as an aromatic carminative. Dose  $\frac{1}{2}$ –3 mins.

#### Oil of Cinnamon Bark.

**Source.**—Under layer of bark of *Cinnamomum zeylanicum*. Yield up to 2%.

**Habitat.**—Mainly Ceylon, but also Jamaica, Seychelles, India, and Mauritius.

**Constituents.**—Cinnamaldehyde 60–75%, eugenol 5–10%, benzaldehyde, methyl amyl ketone, phellandrene, pinene, cymene, nonyl aldehyde, linalool, cumic aldehyde, caryophyllene, esters of isobutyric acid.

**Characteristics.**— $\rho$  0.950–1.03;  $\alpha$  0° to -8°, seldom over -2°;  $n_D$  1.565–1.590. Soluble in 3 vol. 70% alcohol. The B.P. requires:  $\rho$  1.00–1.03;  $\alpha$  0° to -2°;  $n_D$  1.565–1.582. Soluble in 3 vol. of 70% alcohol. Aldehydes 50–65%. The oil is usually distilled in England; that distilled in Ceylon sometimes contains leaf oil. Adulteration with synthetic cinnamaldehyde or with cassia oil distillates has been detected.

**Uses.**—As a spice, both for its flavour and its germicidal properties. R.W. Coefficient, 7–9. Medicinally as a carminative and antiseptic for internal use, and for inhalation. Dose 1–3 mins. In perfumery.

#### Oil of Cinnamon Leaf.

**Source.**—Leaves and twigs of *Cinnamomum zeylanicum*. Yield about 1%.

**Habitat.**—Mainly Ceylon, but also Jamaica, Seychelles, India, and Mauritius.

**Constituents.**—Eugenol 70–95%, cinnamaldehyde and benzaldehyde up to 3%, pinene,  $\alpha$ -phellandrene, dipentene, safrole, methyleugenol, borneol, geraniol, caryophyllene,  $\alpha$ -terpineol, linalool, cinnamyl alcohol.

**Characteristics.**— $\rho$  1.045–1.065;  $\alpha$  -1° to +3° (often too dark for observation);  $n_D$  1.530–1.545. Soluble in 3 vol. of 70% alcohol.

*Uses*.—As a source of eugenol for the manufacture of vanillin. R.W. Coefficient, 7-10.

### Oil of Ceylon Citronella.

*Source*.—*Cymbopogon nardus* (*Andropogon nardus*). Lena batu grass. Yield up to 0.7%.

*Habitat*.—Ceylon, Seychelles.

*Constituents*.—Geraniol 30-40%, citronellal 15-20%, borncol, nerol, camphene, dipentene, limonene, methylcugenol, citronellol, farnesol, methylheptenone, thujone; acetate, butyrate, and valerate esters.

*Characteristics*.— $\rho$  0.898-0.920;  $\alpha$   $-7^{\circ}$  to  $-14^{\circ}$ ;  $n_D$  1.4785-1.4900. Acetyltable constituents 55% min. Soluble in 10 vol. 80% alcohol.

*Uses*.—Perfuming household soaps, polishes, carbide, etc. R.W. Coefficient, about 2.

### Oil of Java Citronella.

*Source*.—*Cymbopogon nardus* (*Andropogon nardus*). Yield up to 0.7%.

*Habitat*.—Java, Burma, Malay.

*Constituents*.—Citronellal 35-50%, citronellol and geraniol 35-45%, citral, dihydrocitronellal, dicitronellol ether, methyleugenol, sesquictronellene.

*Characteristics*.— $\rho$  0.885-0.900;  $\alpha$   $-5^{\circ}$  to  $+1^{\circ}$ ;  $n_D$  1.465-1.473. Acetyltable constituents 80-95%. Non-volatile residuo 2-6%. Soluble in 3 vol. of 80% alcohol. R.W. Coefficient, about 2.

*Uses*.—Perfumery. Source of geraniol and citronellal.

### Oil of Cloves.

*Source*.—Unopened flower buds of evergreen *Eugenia caryophyllata* (*Caryophyllus aromaticus*). Yield 11-20%.

*Habitat*.—Zanzibar, Madagascar, Penang, Pemba.

*Constituents*.—Eugenol 78-98%; acetyl-eugenol up to 17%,  $\alpha$ - and  $\beta$ -caryophyllene, traces of vanillin, benzyl alcohol, methyl amyl carbinol, methyl heptyl carbinol, valeraldehyde, salicylic acid, methyl benzoate, methyl amyl ketone, methyl heptyl ketone, dimethylfurfural.

*Characteristics*.— $\rho$  1.044-1.069;  $\alpha$  up to  $-2.5^{\circ}$ ;  $n_D$  1.528-1.540. Eugenol 80-95%; soluble in 3 vol. 70% alcohol. The B.P. requires:  $\rho$  1.047-1.060;  $n_D$  1.528-1.537. Eugenol 85-95%. Soluble in 2 vol. 70% alcohol.

*Uses*.—Flavouring, preservative, antiseptic. R.W. Coefficient, 8. Manufacture of vanillin and isoeugenol. Medicinally as an expectorant, internal antispasmodic antiseptic, antineuralgic, counter-irritant, and as an antiseptic mild anæsthetic in dentistry. Dose 1-3 mins.

### Oil of Clove Stems.

*Source*.—Leaves and stems of *Eugenia caryophyllata*. Yield 5-6.5%.

*Habitat*.—Zanzibar, Madagascar, Penang, Pemba.

*Constituents*.—As oil of cloves.

*Characteristics*.— $\rho$  1.04-1.07;  $\alpha$  up to  $-1.5^{\circ}$ ;  $n_D$  1.53-1.54. Eugenol 82-95%. The odour of this oil is inferior to that of clove-bud oil.

### Oil of Coriander.

*Source*.—Fruits of *Coriandrum sativum*. Yield up to 1%.

*Habitat*.—Levant, Russia, Central Europe, Morocco.

*Constituents*.— $\alpha$ -Linalool, geraniol, borncol, pinene, cymene, dipentene, terpinolene, phellandrene,  $\gamma$ -terpinene, decaldehyde, acetic and decolic esters.

*Characteristics*.— $\rho$  0.870-0.885;  $\alpha$   $+7^{\circ}$  to  $+14^{\circ}$ ;  $n_D$  1.463-1.476. Soluble in 3 vol. 70% alcohol. Esters 4-23%. Alcohols 60-80%. The B.P. requires:  $\rho$  0.870-0.884;  $\alpha$   $+8^{\circ}$  to  $+15^{\circ}$ ;  $n_D$  1.462-1.472. Soluble in 3 vol. of 70% alcohol.

*Uses*.—In Eau de Cologne, liqueurs, flavours. Medicinally as a carminative stimulant and to prevent griping. Dose 1-3 mins.

### Oil of Dill.

(*Oleum Anethi*.)

*Source*.—Fruit of *Anethum graveolens* (*Peucedanum graveolens*). Yield up to 4%.

*Habitat*.—Central to Southern Europe, India, North East Africa.

*Constituents*.—Carvone 40-65%, phellandrene, limonene, a decatriene, dill-apiole.

*Characteristics*.—The B.P. requires:  $\rho$  0.900-0.915;  $\alpha$   $+70^{\circ}$  to  $+80^{\circ}$ ;  $n_D$  1.481-1.492. Soluble in 1 vol. 90% or 10 vol. 80% alcohol. Carvone 43-63%.

*Uses*.—As an aromatic carminative, especially for infantile flatulence. Dose 1-3 mins. (for adults).

### Oils of Eucalyptus.

(v. Vol. IV, 389d.)

There are over 300 species of Eucalyptus, which form about 75% of the vegetation of Australia. They have been exhaustively studied by R. T. Baker and H. G. Smith ("A Research on the Eucalypts, especially in regard to their essential oils," Sydney, 1920, 2nd ed.) and by Penfold *et al.* (Proc. Roy. Soc. N.S.W. 1923-24). Only a few are distilled for essential oil, namely *E. australiana*, *E. amygdalina*, *E. citriodora*, and *E. dives*.

### Oil of *E. australiana*.

This is the most widely distilled of the eucalyptus oils and is used in pharmacy. It replaces the oil of *E. globulus*, which was formerly the only oil recognised by the B.P. and which was generally a mixture of oils from various species. Partial fractionation of the oil is usually practised to improve its quality.

*Constituents*.—Cincole 70-90%, tasmanol, piperitone, phellandrene, pinene, terpineol, geraniol, citral. Yield 3%.

*Characteristics*.—The B.P. requires:  $\rho$  0.910-0.930;  $\alpha$   $-5^{\circ}$  to  $+5^{\circ}$ ;  $n_D$  1.458-1.470. Soluble in 5 vol. of 70% alcohol. Cincole 70% min. by the cresincol method.

*Uses*.—Pharmacy; R.W. Coefficient, 5. Mineral flotation. Perfuming dentifrices. Inhalations. Internally for catarrhal inflammation of the mucous membranes. Dose 1-3 mins.



*Oil of E. amygdalina.*

Confusion exists over the exact species to which this name refers. The oil of commerce probably arises from all or mixtures of the oils of *E. amygdalina* (black peppermint of Tasmania), *E. amygdalina* (var. *nitida* of N.S.W.) and *E. phellandra* (narrow leaf peppermint of N.S.W.). In commerce the name *amygdalina* is recognised as denoting oils of high phellandrene and low cineole content.

**Constituents.**—Cineole 5-35%, phellandrene, piperitone.

**Characteristics.**— $\rho$  0.86-0.90;  $\alpha$  -15° to -70°;  $n_D$  1.47-1.48. Solubility in alcohol very variable.

*Oil of E. citriodora.*

**Source.**—*E. citriodora* (citron scented gum). Yield up to 1.5%.

**Habitat.**—North Queensland.

**Constituents.**—Citronellal 90-98%, geraniol, pinene.

**Characteristics.**— $\rho$  0.865-0.905;  $\alpha$  -1° to +2°;  $n_D$  1.450-1.468. Soluble in 2 vol. 7% alcohol.

**Uses.**—Perfumery and as a source of citronellal.

*Oil of E. dives.*

**Source.**—*E. dives* (broad leaf peppermint). Yield up to 4%.

**Habitat.**—New South Wales, Queensland.

**Constituents.**—Cineole, piperitone 50%, piperitol, 4-terpinenol, pinene, phellandrene 40%.

**Characteristics.**— $\rho$  0.890-0.907;  $\alpha$  -55° to -80°;  $n_D$  1.479-1.481. Soluble in 1 vol. 80% alcohol. Piperitone 46-53%.

**Uses.**—As a source of piperitone for the manufacture of thymol and menthol. There are at least four varieties of *E. dives* which yield oils of widely different composition. The one commercially available is that in which piperitone predominates, the characteristics for which are given above.

*Oil of Fennel.*

**Source.**—Fruit of *Foeniculum vulgare* (*F. capillaceum*) (*F. dulce*). Yield up to 6%.

**Habitat.**—Russia, Roumania, Greece, Asia Minor, India, Japan.

**Constituents.**—Anethole 60-90%, fenchone, methylchavicol, pinene, dipentene, limonene, phellandrene.

**Characteristics.**— $\rho$  0.96-1.00;  $\alpha$  +4° to +24°;  $n_D$  1.525-1.540;  $F_p$  +3 to +10. Soluble in 1 vol. 90% alcohol.

**Uses.**—As for oil of Star Aniseed.

*Oil of Geranium.*

**Source.**—*Pelargonium capitatum*. *P. radula*. *P. odoratissimum*. *P. graveolens*. Yield up to 2%.

**Habitat.**—Reunion, Algeria, South France, British East Africa, Tanganyika, Spain.

**Constituents.**—Citronellol 40-75%, geraniol 25-60%, nerol,  $\beta$ -phenylethyl alcohol, terpineol, linalool, menthol, menthone, phellandrene, esters of tiglic, acetic, isobutyric, and isovaleric acids.

**Characteristics.**— $\rho$  0.888-0.906;  $\alpha$  -7° to -14°;  $n_D$  1.462-1.472. Acetyl value 200-235. Ester value 40-100. Soluble in 3 vol. 90% alcohol.

**Uses.**—In perfumes of the rose type.

*Oil of Ginger.*

**Source.**—Rhizome of *Zingiber officinale*; *Alpinia galanga*. Yield up to 3%.

**Habitat.**—Jamaica, Cochin China.

**Constituents.**—Zingiberene, camphene, phellandrene, borneol, cineole, citral, zingiberol, decaldehyde, linalool, methylheptenone.

**Characteristics.**— $\rho$  0.874-0.888;  $\alpha$  -30° to -57°;  $n_D$  1.490-1.497. Acetyl value 30-52. Not clearly soluble in 90% alcohol.

**Uses.**—Flavouring. Medicinally as a carminative.

*Oil of Gingergrass.*

**Source.**—Sofia Rosha grass. *Cymbopogon martinii*.

**Habitat.**—Widely in India.

**Constituents.**—Dihydrocumic alcohol (perrylic alcohol), geraniol, carvone, dipentene, limonene, phellandrene.

**Characteristics.**— $\rho$  0.900-0.955;  $\alpha$  -30° to +54°;  $n_D$  1.478-1.495. Soluble in 3 vol. of 70% alcohol. Total alcohols 35-70%. Esters 8-55%.

*Oil of Lavender.*

**Source.**—Flowering tops of *Lavandula officinalis* (*L. vera*, *L. fragrans*, *L. delphinensis*). Yield up to 1%.

**Habitat.**—South France, South England.

**Constituents.**—Linalyl acetate 28-60%, linalool, cineole, borneol, geraniol, coumarin, ethyl amyl ketone, pinene, caryophyllene, esters of acetic, butyric, valeric, and caproic acids.

**Characteristics.**—The B.P. requires:

	French.	English.
$\rho$	0.883-0.895	0.882-0.900
$\alpha$	-3° to -10°	-3° to -10°
$n_D$	1.459-1.464	1.459-1.470
Esters	35% min.	7-12%
Solubility in alcohol	70% 4 vol.	7-12% 4 vol.

**Uses.**—Widely in perfumery. In medicine as a carminative. Dose 1-3 mins. Cf. Oil of Spike Lavender.

*Oil of Lemon.*

**Source.**—By expression of the fresh skins of lemons. *Citrus limonia*.

**Habitat.**—Sicily, South Italy, California.

**Constituents.**—Citral 4-6%, limonene, pinene, camphene, phellandrene, terpinene, octaldehyde, nonaldehyde, citronellal, terpineol, linalyl acetate, methylheptenone, bisabolene, cadinene, citraptene.

**Characteristics.**—

	Sponge extracted.	Machine extracted.
$\rho$	0.856-0.859	0.857-0.860
$\alpha$	+56° to +62°	+56° to +62°
$n_D$	1.474-1.476	
Citral	4.5-6.0%	3-4.5%



The B.P. requires:  $\rho$  0.857–0.861;  $\alpha$  +57° to +65°;  $n_D$  1.474–1.476. Citral 4% min.

Uses.—Flavouring. Perfumery.

### Oil of Lemongrass.

Source.—*Cymbopogon citratus*, *C. flexuosus* (*Andropogon citratus* and *flexuosus*). Yield up to 0.4%.

Habitat.—East India, Ceylon, Strait Settlements, West Indies, Java, Burma, Seychelles, Cochín, Tanganyika.

Constituents.—Citral 70–85%, *n*-decaldehyde, citronellal, methylheptenone, geraniol, terpineol, limonene, cymene, sesquiterpene.

Characteristics.— $\rho$  0.880–0.908;  $\alpha$  –5° to +3°;  $n_D$  1.482–1.489. Solubility 3 vol. 70% alcohol. Oil of Lemongrass is sometimes misnamed Oil of Verbena, which is the oil obtained from *Lippia citriodora*—also known as Melissa Oil.

Uses.—As a source of citral for perfumery.

### Oil of Limes (Distilled).

(p. Vol. VII, 312a)

Source.—*Citrus aurantifolia*.

Habitat.—West Indies (Montserrat, Trinidad, Barbados, Dominica, Martinique).

Constituents.—Citral, limonene, linalool, linalyl acetate, terpineol, cymene.

Characteristics.— $\rho$  0.859–0.869;  $\alpha$  +36° to +52°;  $n_D$  1.476–1.478. Citral up to 2%. This oil is obtained during the concentration of lime juice.

Uses.—Flavouring. Perfumery.

### Oil of Limes (Expressed).

Source.—*Citrus limetta*.

Habitat.—Southern Italy, West Indies.

Constituents.—Citral 6–9%, bisabolene, terpineol, linalool, linalyl acetate up to 25%, citrapteno 9–18%, methyl anthranilate.

Characteristics.— $\rho$  0.878–0.902;  $\alpha$  +30° to +44°;  $n_D$  1.482–1.486.

Uses.—Flavouring and as a substitute for Oil of Lemon.

### Oils of Linaloe.

(v. Vol. VII, 315c.)

Mexican (Bois de citron Mexique).

Source.—Wood and fruit of *Bursera delpechiana* and *B. alaxylon*. Yield up to 3%.

Habitat.—Mexico.

Constituents.—Linalool 50–70%, geraniol, terpineol, methylheptenone, methylheptenol.

Characteristics.— $\rho$  0.875–0.900;  $\alpha$  –15° to +8°;  $n_D$  1.460–1.466. Ester value up to 75. Soluble in 3 vol. 70% alcohol.

Cayenne (Bois de Rose).

Source.—Wood of *Ocotea caudata*. Yield 1%.

Habitat.—French Guiana.

Constituents.—Linalool 60–90%, terpineol 5%, geraniol and nerol 5%, methylheptenone, cineole, dipentene, methylheptenol.

Characteristics.— $\rho$  0.870–0.882;  $\alpha$  –10° to –20°;  $n_D$  1.461–1.466. Ester value 3–7. Soluble in 2 vol. 70% alcohol.

Uses.—Perfumery of Lily of Valley type.

This oil is not to be confused with Oil of Rosewood (Rhodium Oil) distilled from *Convolvulus floridus* and *C. scoparius*, for which the characteristics are:  $\rho$  0.880–0.885;  $\alpha$  –2° to +3°;  $n_D$  1.461–1.468. Soluble in 2 vol. of 70% alcohol.

### Oil of Mustard.

Source.—Ripo seeds of *Brassica nigra* (Black mustard) and *B. juncea*, after freeing from fixed glyceride oil by expression and enzymic fermentation to break down the glucoside sinigrin (potassium myronate). Yield up to 1.25%.

Habitat.—Widely throughout Europe. India, North America.

Constituents.—Allyl isothiocyanate 92–98%, allyl cyanide, carbon disulphide, dimethyl sulphide.

Characteristics.— $\rho$  1.015–1.025. Optically inactive.  $n_D$  1.525–1.528. Boiling range 145–153°.

Uses.—Medicinally as a vesicant and rubefacient in liniments and plasters. As a spice and preservative.

### Oil of Neroli.

Source.—Fresh flowers of *Citrus bigaradia* (*C. aurantium*, *amara*) (bitter orange). Yield up to 0.15%.

Habitat.—Mainly South France, also Portugal, Spain, North Africa.

Constituents.—Linalyl acetate, neryl acetate, linalool, nerol, farnesol, methyl anthranilate, pinene, camphene, limonene, decaldehyde, indole,  $\beta$ -phenylethyl alcohol, terpineol, jasmone, nerolidol, esters of acetic, benzoic, and phenylacetic acids.

Characteristics.— $\rho$  0.870–0.880;  $\alpha$  +1.5° to +7°;  $n_D$  1.4675–1.474. Ester no. 30–70. Soluble in 2 vol. of 70% alcohol.

Uses.—Widely in perfumery, especially in Eau de Cologne and orange flower water.

### Oil of Nutmeg.

(*Oleum Myristicæ*.)

Source.—Dried nuts of *Myristica fragrans* (*M. malabarica*, *M. argentea*). Yield 6–15%.

Habitat.—Moluccas, Penang, Sumatra, Singapore, Ceylon, West Indies.

Constituents.—Terpineol, borneol, geraniol, pinene, dipentene, camphene, myristicin, safrole, eugenol, linalool.

Characteristics.—The B.P. requires:  $\rho$  0.880–0.925;  $\alpha$  +10° to +30°;  $n_D$  1.474–1.488. Non-volatile residuo 3% max. Soluble in 3 vol. 90% alcohol.

Uses.—Confectionery. Perfumery. In pharmacy for spirit of sal volatile. Medicinally as a stimulant for the cerebral cortex and as a carminative. It is poisonous and may produce convulsions. Dose 1–3 mins.

### Oil of Orange.

Source.—Two varieties of oil obtained by expression of the fresh peel of Orange are available. Sweet from *Citrus sinensis* and bitter from *Citrus vulgaris* and *Citrus aurantium amara*.

*Habitat*.—Sicily and Southern Italy, West Indies, South Africa, California.

*Constituents*.—*d*-Limonene 90–95%; decaldehyde; nonyl alcohol; terpineol; linalool; methyl anthranilate; esters of butyric and caprylic acids.

*Characteristics*.—

	Sweet.	Bitter.
$\rho$ . . . . .	0.8485–0.8500	0.853–0.855
$\alpha$ . . . . .	+98° to +100°	+91° to +96°
$n_D$ . . . . .	1.473–1.475	1.473–1.475
Aldehydes . . . . .	1.3–1.6%	1.4–2.5%
Residue . . . . .	1.5–2.5%	2.6–4%
Solubility in 90% alcohol . . . . .	1.8 vol.	1.8 vol.

*Uses*.—In perfumery and as a flavouring agent.

### Oil of Palmarosa.

*Source*.—Motia Roshia or Rusa grass, *Cymbopogon martini* (*Andropogon schoenanthus*); not to be confused with Sofia Roshia grass from which Gingergrass Oil (*q.v.*) is obtained. Palmarosa Oil is also known as East Indian Geranium Oil. Yield 0.3% or up to 2% on dried grass.

*Habitat*.—India, chiefly in the Bombay Presidency, Central Provinces, and the Behars.

*Constituents*.—Geraniol and citronellol 75–95% in a ratio of about 1.4:1. Esters of acetic and caproic acid 12–15%. Dipentene 1%. Methylheptenone; farnesol.

*Characteristics*.— $\rho$  0.885–0.900;  $\alpha$   $-3^\circ$  to  $6^\circ$ ;  $n_D$  1.472–1.478. Soluble in 3 vol. 70% alcohol.

*Uses*.—Perfumery for rose type perfumes.

### Oils of Pennyroyal.

(*Oleum Pulegii*.)

*European*.

*Source*.—*Mentha pulegium*.

*Habitat*.—France, Spain, Sicily, Hungary, and Russia.

*Constituents*.—Pulegone, menthone, menthol, limonene.

*Characteristics*.— $\rho$  0.930–0.960;  $\alpha$   $+13^\circ$  to  $+35^\circ$ ;  $n_D$  1.482–1.487. Soluble in 2 vol. 70% alcohol. Ketones up to 90%, mainly pulegone.

*American*.

*Source*.—Leaves and stalks of *Hedeoma pulegioides*. Yield about 1.5%.

*Habitat*.—North Carolina, Ohio, Tennessee.

*Constituents*.—*l*-Menthone 50%, pulegone 30%, methylcyclohexanone 8%, *d*-isomenthone, *l*-pinene, *l*-limonene, dipentene, a sesquiterpene alcohol.

*Uses*.—Medicinally as an emmenagogue. Dose 1–3 mins.

### Oils of Peppermint.

There are two general types of Oil of Peppermint produced from the fresh flowering tips of (1) *Mentha piperita* mainly in the U.S.A., and (2) *Mentha arvensis* mainly in Japan, China, and Formosa.

*Oil of Mentha piperita*.

Yield up to about 0.5%.

*Constituents*.—*l*-Menthol, menthone,  $\alpha$ -pinene, *l*-limonene, menthyl acetate, menthyl iso-

valerate, cineole, phellandrene, cadinene, dimethyl sulphide, etc.

*Characteristics*.— $\rho$  0.900–0.920;  $\alpha$   $-18^\circ$  to  $-35^\circ$ ;  $n_D$  1.460–1.464. Total menthol 50–62%; menthone 9–19%; esters 5–14% as menthyl acetate. The B.P. requires:  $\rho$  0.902–0.915;  $\alpha$   $-18^\circ$  to  $-30^\circ$ ;  $n_D$  1.460–1.470. Soluble in 4 vol. of 70% alcohol. Esters 4–9%. Free menthol 46% max. The U.S.P. requires:  $\rho^{25}$  0.896–0.908;  $\alpha_D^{25}$   $-23^\circ$  to  $-33^\circ$ ;  $n_D$  1.460–1.471. Soluble in 4 vol. 70% alcohol. Combined menthol 5%.

*English Peppermint Oil*, which has characteristics similar to those of the American oil, is considered to have a superior odour.

*Uses*.—Flavouring and confectionery. Liqueurs. Pharmaceuticals. Toothpaste, etc. Medicinally as a carminative. Dose 1–3 mins.

*Oil of Mentha arvensis*.

Yield up to 2%.

As originally distilled this oil contains up to 85% of free menthol, part of which crystallises out on cooling. The oil normally exported from Japan is the so-called "Dementholised" oil.

*Constituents*.—*l*-Menthol, neomenthol, menthone, menthenone-1, piperitone, pulegone, ethyl amyl carbinol, cineole, 2-hexenyl phenylacetate, menthyl acetate, limonene.

*Characteristics*.—

	Original oil.	Dementholised oil.
$\rho$ . . . . .	0.900–0.910	0.895–0.905
$\alpha$ . . . . .	$-26^\circ$ to $-42^\circ$	$-24^\circ$ to $-35^\circ$
$n_D$ . . . . .	1.458–1.464	1.458–1.465
Total menthol . . . . .	78–92%	40–60%
Combined menthol . . . . .	2–7%	4–14%

*Uses*.—Preparation of menthol. Flavouring. Medicinally as an aromatic stimulant and carminative to relieve flatulence and colic and prevent griping. Its germicidal properties are insignificant. Dose 1–3 mins.

### Oil of Petitgrain.

*Source*.—Leaves and young shoots of *Citrus bigaradia* (*Citrus aurantium, amara*) (bitter orange). Yield up to 0.4%.

*Habitat*.—Paraguay, South France, Mediterranean area.

*Constituents*.—Linalool, nerol, geraniol, terpineol and their acetic esters. Methyl anthranilate, camphene, pinene, limonene, furfural.

*Characteristics*.—

	French oil.	Paraguayan oil.
$\rho$ . . . . .	0.888–0.897	0.885–0.900
$\alpha$ . . . . .	$-1^\circ$ to $-8^\circ$	$-3^\circ$ to $+11^\circ$
$n_D$ . . . . .	1.460–1.470	1.459–1.466
Esters . . . . .	50–70%	35–60%
Solubility in alcohol . . . . .	2 vol. 80%	2 vol. 80%

*Uses*.—Perfumery as a substitute for the finer Oil of Neroli.

### Oil of Pimento.

(Allspice.)

*Source*.—Fruit of *Pimenta officinalis* (*Eugenia pimenta*). Yield 3–5%.

*Habitat*.—West Indies (Jamaica), Mexico, Costa Rica, Venezuela.

**Constituents.**—Eugenol 65–80%, methyl-eugenol, cincole, phellandrene, caryophyllene.

**Characteristics.**— $\rho$  1.025–1.055;  $\alpha$   $-1^\circ$  to  $-4^\circ$ ;  $n_D$  1.525–1.535. Soluble in 2 vol. 70% alcohol.

**Uses.**—Flavourings. Medicinally as a carminative and with aperients. Dose 1–3 mins.

### Oil of Pine.

**Source.**—Stump wood of *Pinus palustris* (Long leaf pine).

**Habitat.**—U.S.A.

**Constituents.**—Terpineol 50–70%, borneol 5–10%, fenchyl alcohol 5–10%, camphor, anethole, methylchavicol, cineole, dihydroterpinol, sesquiterpenes.

**Characteristics.**— $\rho$  0.925–0.945;  $\alpha$   $-12^\circ$  to  $+9^\circ$ ;  $n_D$  1.475–1.485. Boiling range 180–250°. Soluble in 2 vol. 70% alcohol.

**Uses.**—Disinfectants. Varnish. Perfumery. Mineral flotation. Textile manufacture. Wet-ting agent.

This oil is known in the trade as "Hereules Pine Oil" and "Yarmor Pine Oil."

### Oils of Pine Needles.

There are many varieties of Pine-Needle Oil but they can be classified in three main classes typified by (1) *Abies sibirica*, (2) *Pinus sylvestris*, (3) *Pinus pumilio*. Pine-needle oils differ from the turpentine oils in having a relatively high proportion of oxygenated constituents.

#### Oil of *Abies sibirica* (Siberian Fir) Oleum abietis B.P.

**Habitat.**—North East Russia.

**Constituents.**—Bornyl acetate 30–40%;  $\alpha$ -pinene,  $\beta$ -pinene, camphene, phellandrene, dipentene, bisabolene, santene, terpinyl acetate. Yield about 13%.

**Characteristics.**— $\rho$  0.900–0.928;  $\alpha$   $-30^\circ$  to  $-45^\circ$ ;  $n_D$  1.467–1.476. Soluble in 1 vol. 90% alcohol. The B.P. requires:  $\rho$  0.905–0.925;  $\alpha$   $-32^\circ$  to  $-45^\circ$ ;  $n_D$  1.466–1.476. Bornyl acetate 33–45%.

**Uses.**—Pine oil perfumes. Inhalant.

#### Oil of *Pinus sylvestris*.

**Habitat.**—Central Europe.

**Constituents.**— $\alpha$ -Pinene, dipentene, sylvestrene, bornyl acetate, terpinyl acetate, cadinene. Yield about 15%.

**Characteristics.**— $\rho$  0.870–0.920;  $\alpha$   $-7^\circ$  to  $-22^\circ$ ;  $n_D$  1.475–1.485. Esters 2–15%.

#### Oil of *Pinus pumilio*.

**Source.**—Twigs of *Pinus pumilio* (*P. montana*). Yield up to 0.75%.

**Habitat.**—Austria.

**Constituents.**—Phellandrene, pinene, bornyl acetate 5–10%, pumilone, cadinene, dipentene.

**Characteristics.**— $\rho$  0.860–0.875;  $\alpha$   $-5^\circ$  to  $-15^\circ$ ;  $n_D$  1.470–1.485. Soluble in 10 vol. 90% alcohol.

**Uses.**—Perfumery. Medicinally as an expectorant and inhalant for bronchitis and laryngitis; also as a rubefacient for rheumatism. Dose 1–5 mins.

### Oil of Roses.

(Otto or Attar of Rose.)

**Source.**—*Rosa damascena*, *R. alba*, *R. moschata*, and *R. centifolia*. Yield up to 0.04%.

**Habitat.**—Bulgaria, South France.

**Constituents.**—Citronellol, geraniol, nerol, farnesol,  $\beta$ -phenylethyl alcohol, neral, citral, eugenol, esters, steareptene.

**Characteristics.**— $\rho$  0.849–0.862;  $\alpha$   $-1^\circ$  to  $-4^\circ$ ;  $n_D^{25}$  1.460–1.465. F.p. 19–22°. Steareptene 15–20%. (M.p. 33–37°.) Alcohols 66–78% Citronellol 25–40%.

**Uses.**—Widely in perfumery.

### Oil of Rosemary.

**Source.**—Flowering tops and leaves of the shrub *Rosmarinus officinalis* and hybrids. Yield up to 2%.

**Habitat.**—Mediterranean districts; France, Spain, Dalmatia, Tunis, Greece.

**Constituents.**—Borneol 8–20%; bornyl acetate up to 5%;  $\alpha$ -pinene, cineole, camphene, camphor.

**Characteristics.**— $\rho$  0.890–0.922;  $\alpha$   $-6^\circ$  to  $+13^\circ$ ;  $n_D$  1.465–1.473. Soluble in 10 vol. 80% alcohol. The B.P. requires:  $\rho$  0.900–0.919;  $\alpha$   $-5^\circ$  to  $+10^\circ$ ; 1.464–1.476. Soluble in 1 vol. 90% and 10 vol. 80% alcohol. Esters 2% min. Borneol 9% min.

**Uses.**—Perfumery of the Eau de Cologne type and for hair lotions as Spiritus Rosmarini. The oil has been subjected to much adulteration in the past.

### Oil of Sandalwood.

East Indian Oil (Oleum Santali).

**Source.**—Heart wood of the evergreen *Santalum album*. Yield 2.5–8.5%.

**Habitat.**—The high altitudes of Mysore, Madras, Bombay.

**Constituents.**—Santalol 90–97%, santene, santenone, santalone, santenol, teresantalol,  $\alpha$ - and  $\beta$ -santalenes, santalal, nortricycloeksantalal, santalic acid, teresantelic acid, santalenic acid.

**Characteristics.**— $\rho$  0.973–0.985;  $\alpha$   $-15^\circ$  to  $-21^\circ$ ;  $n_D$  1.503–1.510. Soluble in 5 vol. 70% alcohol at 20°. Esters 4–6.5%. Viscosity at 20° about 138 centipoises.

#### West Australian Oil (Oleum Santali Australiensis).

**Source.**—Wood of the large bush *Fusanus spicatus* (*Santalum cygnorum*; *S. spicata*; *Eucarya spicata*). Yield about 2%.

**Habitat.**—In the west and mid-continent of Australia.

**Constituents.**— $\alpha$ - and  $\beta$ -fusanol over 90%.

**Characteristics.**— $\rho$  0.970–0.976;  $\alpha$   $-3^\circ$  to  $-10^\circ$ ;  $n_D$  1.498–1.508. Soluble in 3–6 vol. of 70% alcohol.

**Uses.**—Until recent times the East Indian oil from *S. album* was the only one recognised by the pharmacopœias. The West Australian oil from *S. australiensis* is now similarly recognised. Phenol coefficient about 1.5. Medicinally for cystitis and gonorrhœa. Dose 5–15 mins. Oils of Sandalwood are used in perfumery on account of their odour and fixative properties.

## Oil of Sassafras.

*Source*.—Roots and bark of *Sassafras officinale* (*Laurus sassafras*). Yield up to 9%.

*Habitat*.—Virginia, Carolina, Tennessee, Canada.

*Constituents*.—Safrole 80%, phellandrene 10%, camphor 7%, cadinene 3%, eugenol.

*Characteristics*.— $\rho$  1.068–1.082;  $\alpha$  +1° to +5°;  $n_D$  1.525–1.831. Ester value up to 2. Soluble in 2 vol. 90% alcohol.

*Uses*.—Medicinally as a rubefacient and anodyne liniment and to destroy pediculi. Dose 1–5 mins. Perfume for soap base and household soap.

## Oil of Shul (Ho).

*Source*.—Uncertain, probably the Shu Sho Boku or "Stinking Camphor tree," a species of *Cinnamomum* or *Machilus*.

*Habitat*.—Formosa.

*Constituents*.—Linalool 60–90%, eugenol, safrole, camphor, cineole, pinene, dipentene, linalyl acetate.

*Characteristics*.— $\rho$  0.870–0.895;  $\alpha$  –1° to –16°. Ester value up to 30.

*Uses*.—Perfumery.

## Oil of Spike Lavender

(Aspic).

*Source*.—*Lavandula latifolia* (*L. spica*; *L. vulgaris*). Yield up to 1%.

*Habitat*.—South France and Spain.

*Constituents*.—Borneol, linalyl acetate, linalool, camphor, geraniol, cineole 33–40%, terpineol.

*Characteristics*.—

	French.	Spanish.
$\rho$	0.900–0.921	0.903–0.922
$\alpha$	–4° to +7°	–5° to +12°
$n_D$	1.464–1.468	1.464–1.470
Ester value	3–22	4–27
Alcohols	25–40%	—
Solubility in 70% alcohol	3 vol.	3 vol.

*Uses*.—Perfumery. Pottery glazes. As an insect repellent. Cf. Oil of Lavender.

## Oil of Star Aniseed.

*Source*.—Fruit of *Illicium verum*. Yield up to 6%.

*Habitat*.—Kwangsi, South China; Hainan.

*Constituents*.—Anethole 90%, Methylchavicol, *p*-propenylphenol, limonene, pinene, anisaldehyde, anise ketone, phellandrene, terpineol, safrole, bisabolene, cadinene.

*Characteristics*.— $\rho$  0.975–0.990;  $\alpha$  –2° to +1°;  $n_D$  1.550–1.560. F.p. 15–19°. Soluble in 3 vol. 90% alcohol.

## Oil of Thyme.

*Source*.—Many species of *Thymus*, mainly *T. zygis* (*gracilis*), *T. vulgaris* (Spanish Tomillo), and *Ocimum viride*. Yield up to 2%.

*Habitat*.—Spain, Portugal, South France, Crete.

*Constituents*.—Thymol, carvacrol, borneol, terpinenol, geraniol, linalool, menthene, camphene, cymene, terpinene.

*Characteristics*.— $\rho$  0.915–0.955;  $\alpha$  –4° to +2°;  $n_D$  1.49–1.51. Phenols 30–50%. Soluble in 2 vol. of 80% alcohol. The ratio of thymol to carvacrol varies considerably.

*Uses*.—Perfumery. Deodorants and germicides. R.W. Coefficient, about 14. Medicinally as an antiseptic carminative and anthelmintic and for the treatment of whooping cough and bronchitis. Dose 1–5 mins.

## Oil of Turpentine.

Turpentine varies widely in composition. There are four types recognised industrially:

1. *Gum Spirits of Turpentine*.—Obtained by steam distilling the oleo-resin exudation from various conifers, such as *Pinus palustris*, *P. hetero-phylla*, and *P. maritima*, consisting mainly of  $\alpha$ -pinene.

2. *Wood Turpentine*.—Obtained by steam distilling chips and stumps, consisting largely of dipentene.

3. *Wood Turpentine*.—Obtained by destructive distillation of chips and stumps.

4. *Sulphite Turpentine*.—Obtained as a by-product in the manufacture of paper pulp from wood and consisting largely of carene.

## A.S.T.M. SPIRITS OF TURPENTINE, D13-14.

	Gum spirits of turpentine.		Wood turpentine.					
			Steam distilled.		Sulphate.		Destructively distilled.	
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
$\rho_{15}^{\circ}$	0.875	0.860	0.875	0.860	0.875	0.860	0.866	0.860
$n_D^{20}$	1.478	1.465	1.478	1.465	1.478	1.465	1.483	1.463
Residue after polymerisation with 38N-H <sub>2</sub> SO <sub>4</sub> , Vol. %	2	—	2	—	2	—	2	—
$n_D^{20}$	—	1.500	—	1.500	—	1.500	—	1.480
Initial B.p./760 mm., °C.	160	150	160	150	160	150	157	150
% distilling below 160°C./760 mm.	—	90	—	90	—	90	—	60
% distilling below 180°C./760 mm.	—	—	—	—	—	—	—	90

The following grades are recognised\* :

*British Standard Turpentine, Type 1, No. 244, 1936*, consists of refined gum spirits of turpentine having the following characteristics:  $\rho$  0.862–0.872; B.R. below 150°C. 1% max.; below 170°C. 95% min. Residue 3% max.  $n_D$  1.469–1.478. Residue unpolymersisable by sulphuric acid, 11% max. F.p. 90°F. min.

*British Standard Turpentine, Type 2, No. 290, 1936*, is distilled from oleo-resins or wood by steam or destructive distillation, and has  $\rho$  0.859–0.875; B.R. below 150°, 1% max.; below 170°, 70% min.; below 180°, 90% min. Residue 2% max.  $n_D$  1.463–1.483.

The American Society for Testing Materials recognises all four of the varieties described above, the specifications being as given in the table opposite.

### Oil of Vetiver.

*Source*.—Roots of Indian couch-grass or *Cuscuta*, *Vetiveria zizanioides* (*Andropogon muricatus*; *A. squarrosus*; *V. muricatus*).

*Habitat*.—Mainly in British India, Malay States, Ceylon. Also in Java, West Indies, Brazil, Seychelles, Reunion, Gold Coast.

*Constituents*.—Mainly sesquiterpenes, viz. vetivene, vetiverone, vetivenol, and esters.

*Characteristics*.— $\rho$  0.98–1.03;  $\alpha$  +20° to +39°;  $n_D$  1.51–1.53. Soluble in 2 vol. 80% alcohol (turbid with more).

*Uses*.—Perfumery as an odoriferous constituent and as a fixative. Medicinally in India by the Ancients. The distillation is

\* The British and American specifications quoted below are given in an abbreviated form suitable for quick reference only. For a proper understanding of the figures it is necessary to consult the detailed specifications which can respectively be obtained from the British Standards Institution, 28 Victoria Street, London, S.W.1, and the American Society for Testing Materials, 260, South Broad Street, Philadelphia, U.S.A., who own the copyrights.

mainly done in Europe from imported roots. Yield up to 3.3% (dry basis). Average oil percentage in distillate 0.02.

### Oil of Wintergreen.

(Sweet Birch, *Oleum Betulæ*.)

*Source*.—Leaves of herb *Gaultheria procumbens* (Wintergreen) (Tea berry). Bark of tree *Betula lenta* (Sweet Birch).

*Habitat*.—U.S.A., New England, Illinois, Alleghany.

*Constituents*.—Methyl salicylate with traces of other esters, an alcohol, ketone, and aldehyde.

*Characteristics*.— $\rho$  1.180–1.189;  $\alpha$  –3° to +0.5°;  $n_D$  1.534–1.538. Soluble in 5 vol. 70% alcohol. Methyl salicylate 98% min.

*Uses*.—Flavouring for chewing gum, tooth-pastes. Medicinally for rheumatism and sciatica. Dose 5–15 mins. R.W. Coefficient, 0.4.

### Oil of American Wormseed.

(*Oleum Chenopodii*.)

*Source*.—Flowers and fruits of *Chenopodium ambrosioides* var. *anthelminticum* (Baltimore Oil). Yield up to 1%.

*Habitat*.—Maryland, U.S.A., West Indies.

*Constituents*.—Ascaridole, cymene, l-limonene, sylvestrene, camphor, safrole,  $\alpha$ -terpinene, menthadiene.

*Characteristics*.—The B.P. requires:  $\rho$  0.962–0.983;  $\alpha$  –4° to –8°;  $n_D$  1.474–1.479. Ascaridole 65% min. Oils of inferior quality may result from the decomposition of the ascaridole due to unsuitable methods of distillation.

*Uses*.—Medicinally as an anthelmintic for hook-worm and round-worm. Dose 3–15 mins. It is poisonous; toxic symptoms are transient dizziness and vomiting; a purgative should be used as an antidote.

T. H. D.

# INDEX TO VOLUME VIII

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